J. Phys. Chem. A **1997,** *101,* 4437−4443

Theoretical Investigation of Thiophene Oligomers: A Spin-Coupled Study

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Received: January 6, 1997; In Final Form: April 3, 1997[⊗]

The electronic structure of thiophene oligomers is analyzed within the framework of spin-coupled theory. The π valence electrons are correlated for either one or two central thiophene rings embedded in oligomers ranging up to six units. The localized nature of the spin-coupled orbitals, together with a proper account of the embedding, makes it possible to obtain a set of orbitals which can be transferred from smaller oligomers to larger ones. In this way, we obtain orbitals that may be considered a good approximation to those of the polymer.

I. Introduction

The structural and electronic properties of polythiophene and its derivatives, doped or otherwise, have received a great deal of attention in the last two decades, with particular interest in gaining an understanding of their electric and nonlinear optical properties.[1] Theoretical investigations have contributed significantly to this goal. Extensive analyses of the structure and of the vibrational and electronic spectra of thiophene oligomers (see, e.g., refs 2−13) have been performed both at ab initio and semiempirical levels. In some cases it has proved possible to extrapolate theoretical results to long chains. However, ab initio calculations are severely limited by the dimensions of such systems, and only very short thiophene oligomers have been investigated. Fortunately, recent experimental investigations have demonstrated some similarity between polythiophene and small oligomers, such as quinquethiophene and sexithiophene,[14,15] thus encouraging the pursuit of accurate analysis of such short chains. The treatment of electron correlation effects in these systems has typically been limited to the π valence electrons,[10] but this is probably not a drastic limitation, the electric properties of polyconjugated systems being generally ascribed to the π electrons only.

In this work, we present a contribution to the understanding of the electronic structure of neutral oligomers by means of spin-coupled (SC) theory.[16,17] This method has previously been applied successfully to the study of a wide range of small organic and inorganic molecules.[17] The spin-coupled approach incorporates a considerable degree of nondynamical electron correlation while permitting a direct description of the key features of electronic structure in terms of well-established chemical concepts. Now, as part of our attempts to extend to larger systems the range of applicability of the spin-coupled method, we analyze here the possibility of transferring spin-coupled orbitals from small molecules to much larger ones.

For this purpose, we take advantage of the localized nature of the spin-coupled orbitals, which should allow us to generate accurate descriptions of larger oligomers starting from the knowledge only of smaller "building blocks". The dimension of such building blocks is one of the key issues in this work. The spin-coupled description of the isolated thiophene molecule is already well established.[18] In spite of their localized nature, it will be shown that the orbitals for the monomer cannot be considered a good approximation to those of the polymer because of the lack of a proper description of the effects of neighboring rings.

In this paper, we report a series of spin-coupled calculations on thiophene oligomers in which either one or two central rings are treated at the spin-coupled level, with the "boundary" effects taken properly into account at a lower level of theory. We feel confident that the orbitals obtained for the largest systems studied here may be considered a good approximation to the spin-coupled orbitals of the polymer. To substantiate this, we show how the spin-coupled orbitals can be transferred from smaller oligomers to larger ones without appreciable loss of nondynamical correlation energy. All of this has been made possible by the particular computational scheme reported in this work, which makes accurate spin-coupled calculations feasible for much larger systems than hitherto.

The most dramatic properties of pure and doped polythiophene are of course connected with its electric and associated optical properties. These we have not treated in this paper—they remain the subject of a future investigation. However, it is worth observing that the electrical conductivity of the single crystal of pure hexamer[19] must involve electron transfer both *within* the oligomer unit and *between* the units. This last can be treated by a method similar to that of Davydov's treatment of excitons in molecular crystals.[20]

II. Method

In this section, we review briefly only the main aspects of spin-coupled theory particularly relevant to the present work; much more complete accounts of the theory and computational methodology, and of its applications, may be found in numerous places.[16] The spin-coupled wave function for a system of N valence or "active" electrons and $2n$ core or "inactive" electrons can be written in the form

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[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1997.

$$\Psi_{SM} = \mathcal{A}\ (\varphi_1\varphi_1...\varphi_n\varphi_n\Theta^{2n}_{\mathrm{pp}}\phi_1\phi_2...\phi_N \sum_k^{f_S^N} c_{Sk}\Theta^N_{SM;k}) \quad (1)$$

in which $\mathcal{A}$ is the antisymmetrizing operator, φ_i and ϕ_i are the ith core and valence spin-coupled orbitals, respectively. $\Theta^{2n}_{\mathrm{pp}}$ stands for the spin eigenfunction representing the perfect pairing of a system of $2n$ core electrons, and $\Theta^N_{SM;k}$ is the kth spin eigenfunction, corresponding to S and M quantum numbers, for the space of dimension f_S^N spanned by the spins of the N valence electrons. The weight of this spin eigenfunction to the total spin-coupled wave function is determined by the c_{Sk}, which are usually denoted spin-coupling coefficients.

In general, the core and spin-coupled valence orbitals and the spin-coupling coefficients are determined variationally without imposing any constraints that alter the overall wave function.[21] It can be shown that the wave function is invariant to normalization of the orbitals, to orthogonalization of the core orbitals amongst themselves, and to orthogonalization of the spin-coupled valence orbitals to the core. The resulting spin-coupled orbitals for the active electrons are unique, in the sense that they cannot be subjected to general linear transformations without modifying the total wave function. In many applications, including the present one, it is an acceptable approximation to use frozen core orbitals, taken without further optimization from a prior self-consistent field (SCF) or complete active space SCF calculation. In some cases, it proves most useful for this purpose to use localized molecular orbitals (LMOs) rather than the canonical (MOs).

In the present work, we found it convenient to carry out calculations according to the following procedure: starting from the choice of a basis set of dimension m, we perform a standard closed-shell SCF calculation and localize the resulting canonical MOs using an implementation of the overlap or population criterion of Pipek and Mezey.[22] Subsequently, we may classify the resulting MOs as n inactive ("core"), $^1/_2N$ active ("valence"), and $m - n - {}^1/_2N$ unoccupied ("virtual") orbitals, in which the active orbitals accommodate the π valence electrons in the central one or two rings to be treated explicitly at the spin-coupled level. For each oligomer, it proves straightforward to identify the three (or six) valence LMOs of π symmetry for the central one (or two) ring(s). The spin-coupled valence orbitals may then be expanded in the set of all the LMOs except the doubly occupied core LMOs

$$\phi_i = \sum_{j=n+1}^{m} b_{ij}\varphi_j \equiv \sum_{\mu=1}^{m} t_{\mu i}\chi_\mu$$

in which $\{\chi\}$ is the atomic orbital basis set. In this way, the resulting spin-coupled orbitals are fully expanded in the basis space orthogonal to the core.

The expectation value of the energy corresponding to the spin-coupled wave function (1) assumes the following form

$$E = \langle\Psi|H|\Psi\rangle = E_{\mathrm{core}}[\varphi] + E_{\mathrm{core/valence}}[\varphi,\phi] + E_{\mathrm{valence}}[\phi] \quad (2)$$

in which H is the usual nonrelativistic electronic Hamiltonian. This expression can be rearranged as

$$E = \sum_{i,j}^{N} \langle\phi_i|h_{\mathrm{eff}}|\phi_j\rangle D(i|j) + {}^1/_2 \sum_{i,j,k,l}^{N} \langle\phi_i\phi_j|\phi_k\phi_l\rangle D(ij|kl) \quad (3)$$

where $\langle\phi_i|h_{\mathrm{eff}}|\phi_j\rangle$, $\langle\phi_i\phi_j|\phi_k\phi_l\rangle$ are one- and two-electron integrals, and $D(i|j)$, $D(ij|kl)$ are one- and two-particle density matrices that depend only on the N valence (active) electrons. h_{eff} represents an effective one-electron Hamiltonian which incorporates the effect of the $2n$ core (inactive) electrons. Its usual representation

$$\langle\phi_i|h_{\mathrm{eff}}|\phi_j\rangle = \sum_{\mu,\nu}^{m} t_{\mu i}t_{\nu j}F^{(n)}_{\mu\nu}$$

$$F^{(n)}_{\mu\nu} = \langle\chi_\mu|h|\chi_\nu\rangle + {}^1/_2\sum_{k=1}^{n}[2\langle\varphi_k\chi_\mu|\varphi_k\chi_\nu\rangle - \langle\varphi_k\varphi_k|\chi_\mu\chi_\nu\rangle] \quad (4)$$

corresponds to the elements of the Fock matrix for the n SCF core MOs.

Exploiting the fact that $F^{(n)}_{\mu\nu}$ depends only on the frozen core MOs and remembering that we correlated only the valence electrons with π symmetry for the central ring(s), we devised a powerful scheme which allowed the investigation of relatively large systems for which the total number of basis functions exceeded the thresholds fixed by usual packages that rely on storing integrals on disk. Our strategy involves the following steps: (1) perform a closed-shell SCF (RHF) calculation using a direct SCF procedure;[23] (2) localize the canonical MOs, as described above; (3) using these LMOs, build the Fock matrix for the $2n$ electron system that excludes the N valence π electrons for the central ring(s); (4) assemble the one-electron integrals given by eq (4) corresponding only to π MOs; (5) by means of a traditional integral package,[23] generate only the two-electron integrals corresponding to π symmetry and carry out the corresponding 4-index transformation.

By means of this approach, the number of basis functions to be handled in the spin-coupled calculations is drastically reduced: in the case of the hexamer, for example, the 6-31G basis of 358 functions reduces to the "spin-coupled active set" of 60 basis functions of π symmetry.

A further refinement of the converged spin-coupled wave function is the addition of structures which include excitations to orbitals that are not occupied in the ground state. This is known as a "nonorthogonal configuration interaction" calculation or the spin-coupled valence bond (SCVB) approach. At convergence, each spin-coupled orbital satisfies an equation which may be recast in the form[24]

$$\hat{F}^{(\mathrm{eff})}_\mu\,\phi_\mu = \epsilon_\mu\phi_\mu \qquad \mu = 1, 2, ..., N$$

The $\hat{F}^{(\mathrm{eff})}_\mu$ operators are constructed from quantities in which spin-coupled orbital ϕ_μ is missing. This gives a good representation of the physical situation in which an electron in ϕ_μ "moves" in the field of the other $N - 1$ electrons. Each operator $\hat{F}^{(\mathrm{eff})}_\mu$ is Hermitian and possesses a complete set or stack of orthonormal orbitals $\phi^{(i)}_\mu$ ($i = 0, 1, 2, ..., m - 1$), where m is the dimension of the basis set. One of the orbitals in each stack, say $\phi^{(0)}_\mu$, corresponds to the occupied spin-coupled orbital, already found at convergence of the variational procedure for minimizing the energy. Orbitals from different stacks may overlap unless they belong to different irreducible representations of the molecular point group. In addition to providing quantitative refinement of the ground state, configurations generated by excitations to these virtual orbitals have proved very powerful to describe excited states,[24] and we expect them to be useful to describe transport properties of polymers.

III. Computational Details

We have performed calculations on a series of thiophene oligomers with up to six rings. In keeping with X-ray diffraction

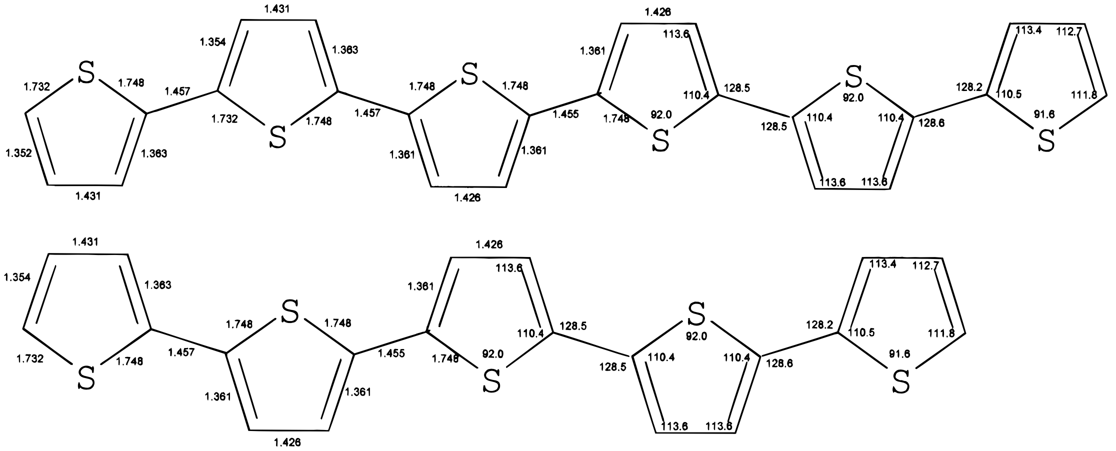


Figure 1. SCF-optimized geometry of quinquethiophene and sexithiophene (distances in angstroms, angles in degrees).

TABLE 1: SCF and SC Energies of the Oligomers at the SCF-Optimized Geometries Described in the Text[a]

	(6-31G basis)		(6-31G* basis)	
number of rings	SCF energy (au)	SC energy (au)	SCF energy (au)	SC energy (au)
1	−551.187 495	−551.243 637	−551.289 990	−551.342 584
2	−1101.227 366	−1101.338 334	−1101.429 292	−1101.533 313
3	−1651.267 940	−1651.318 922	−1651.569 001	−1651.617 133
4	−2201.308 466	−2201.413 603	−2201.708 771	−2201.807 739
5	−2751.349 292	−2751.399 843		
6	−3301.389 808	−3301.494 517		

[a] The SC calculations correlated six electrons for the systems with odd numbers of rings and twelve electrons for the systems with even numbers of rings.

results on powders[25] and single crystals,[26] we have chosen the all-anti conformation. Previous full SCF optimizations of 2,2′-bithiophene using polarized basis sets[4,13] found a value of ∼150° for the dihedral angle formed by the two rings, in agreement with electron diffraction results on the gas molecule.[27] However, the flatness of the potential curve as a function of the torsion angle ensures that this deviation from planarity is not energetically relevant and that the assumption of an antiplanar structure ($\theta = 180°$) does not involve significant errors.

For the first four members of the series we have used geometries optimized employing MIDI−4 basis sets for carbon and hydrogen atoms[28] and a MIDI−4* basis for the sulfur atoms,[29] reported in the literature.[3] In the case of quinquethiophene and sexithiophene we have performed a new optimization with the same basis sets, imposing C_{2v} and C_{2h} symmetries, respectively. The resulting geometries for these two molecules are reported in Figure 1.

All the subsequent SCF and SC calculations were carried out employing the 6-31G basis set[30] but, to check the importance of polarization functions on the heavy atoms for the first four oligomers, we also investigated the importance of adding *d* functions on carbon and sulfur, with exponents 0.8 and 0.65, respectively (6-31G* basis).

Using the procedure outlined above, spin-coupled calculations were carried out explicitly for the six (odd-ring oligomers) or twelve (even-ring oligomers) π valence electrons of the central ring(s). It must be stressed that in this way the “core” is constituted by all the σ electrons, the $2p_\pi$ inner electrons on sulfur, and by the π valence electrons of the external rings. This allows a correlated spin-coupled description of the central unit “embedded” in a proper core described at the *all-electron* SCF level of theory.

Further series of calculations were carried out with the aim of elucidating the role of sulfur in the chemistry of thiophene oligomers, as well as the possible additivity of sulfur and carbon atom contributions to the spin-coupled correlation energy. For this purpose, two different sets of spin-coupled calculations were then performed: (a) By including in the “core” all the LMOs describing valence π electrons on sulfur we correlated explicitly the π electrons of the carbon atoms of one, two, or three rings at various levels of “embedding” and (b) vice versa, by “freezing” into the core the LMOs describing the π electrons of the carbon atoms, various sets of valence π electrons of the sulfur atoms were correlated at the spin-coupled level, embedded in “cores” of increasing size.

The full spin space was utilized in all of the spin-coupled calculations, with f_S^N ranging from 1 to 132 when going from the two- to the twelve-electron cases.

To analyze the possibility of “transferring” orbitals from one system to another, as expected by chemical intuition and so clearly expressed by classical valence bond theory, we determined the percentage of nondynamical electron correlation recovered for a given system using sets of spin-coupled orbitals transferred from smaller oligomers.

Following our standard procedure,[16] after converging on the spin-coupled solutions we have generated stacks of virtual orbitals and then performed some selected SCVB calculations which included excitations into them. The SC and SCVB calculations were carried out by means of our own programs which compute efficiently all of the required density matrices;[16,31] for the SCF calculations we used the Gamess (US) package.[23]

IV. Results and Discussions

Calculations on the oligomers with up to four rings were carried out using both the 6-31G and 6-31G* basis sets; the orbital pictures emerging from these results are practically identical. Consequently, the study of the larger systems was performed employing only the 6-31G basis set. In the following, apart from the SCF and SC energy values reported in Table 1, we shall discuss only the results obtained with the smaller basis set.

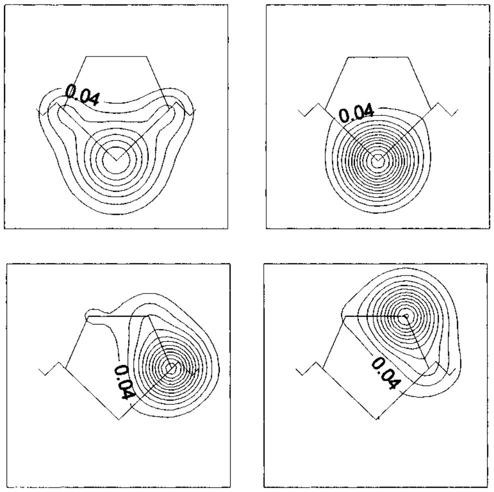
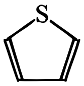


Figure 2. Plots of the symmetry-unique SC orbitals of the central ring of the pentamer.

Odd oligomers. In Figure 2 we present plots of the symmetry-unique spin-coupled orbitals of the five-ring oligomer. Orbitals ϕ_1 and ϕ_2 represent the π lone pair of the sulfur atom: the first of these is a three-center orbital localized on the sulfur atom and on the two adjacent α carbon atoms and the other is much more tightly localized on sulfur with only slight deformations toward the α carbon atoms. Orbitals ϕ_3 and ϕ_4 are localized on the α and β carbon atoms and are reciprocally polarized.

The analysis of the spin couplings reveals that the perfect pairing (I) is dominant, recovering 93.6% of the spin-coupled energy, but also that the pairing corresponding to the structure (II) of the central ring has a weight which cannot be neglected. Resonance between these structures is important for the aromatic properties of thiophene.



(I)

(II)

The spin-coupled orbitals for the central ring in the smaller systems (monomer and trimer) are almost indistinguishable from those obtained for the pentamer. An analysis of the overlaps between corresponding spin-coupled orbitals of the trimer and of the pentamer gives values very close to unity.

This similarity might seem to indicate an almost complete transferability of the orbitals between the different oligomers, suggesting that embedding effects are negligible. In order to investigate more thoroughly this aspect, we have computed the energy of the trimer using the spin-coupled orbitals determined for the monomer, a calculation which we shall indicate as “1 in 3”, and the energy of the pentamer using the spin-coupled orbitals of the trimer, i.e., a “3 in 5” system. Of course, we expect these values of the energy to be worse than those obtained by direct spin-coupled optimization on the host system, but the result obtained is very interesting: the 1 in 3 system recovers only 63% of the spin-coupled energy, but with the 3 in 5 system this result improves to 98%. These results, taken together, support the importance of including the embedding effects from the lateral rings when trying to determine the spin-coupled orbitals of the polymer. The results indicate that it is sufficient to include one ring on each side: the addition of further rings is of negligible importance.

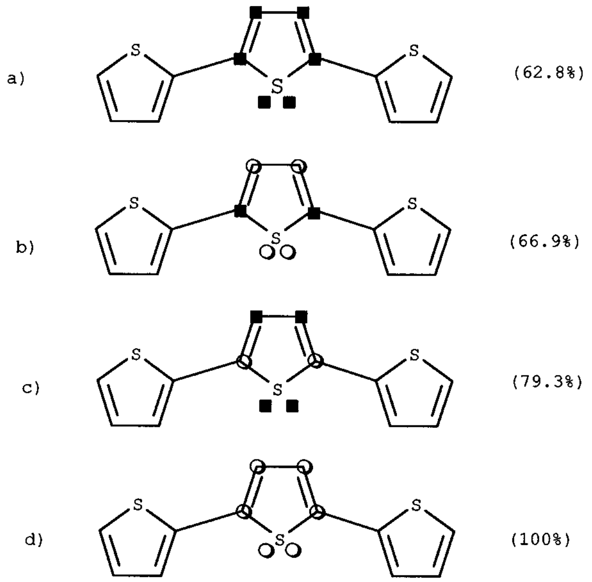


Figure 3. Schematic representation of the transferability of the orbitals from the monomer to the trimer. The SC energy is computed for the trimer, using two different sets of orbitals: the solid squares represent the SC orbitals optimized for the monomer, the empty circles the SC orbitals optimized for the trimer. In parentheses we give the percentage of the SC correlation energy of the trimer (case d).

The consequences of the small differences in geometry were investigated in the case of the 1 in 3 system. To this end, we performed a 1 in 3 calculation using the spin-coupled orbitals determined for the monomer at the geometry of the central ring in the trimer. Once again only 63% of the correlation energy is recovered, showing that the small changes in the geometry do not bias the results reported above.

These various results emphasize also that the overlap between two sets of orbitals might not be a proper indication of their suitability to reproduce the energy: the orbitals of the monomer and of the trimer, for example, have an overlap close to unity, but they provide different estimates of the energy of the pentamer. This fact clearly demonstrates that even small differences in the orbitals can give rise to significant errors and that great care must be paid to determine truly transferable orbitals. This basic problem is well known to people working in density functional theory, where it is now clear that small changes in the total electron density may be responsible for large variations in the energy.

We summarize in Figure 3 the results of calculations performed on the trimer, gradually replacing its spin-coupled orbitals with those of the monomer. As expected on physical grounds, we found that the effect of the interactions from the embedding systems is mainly incorporated into the modifications to the spin-coupled orbitals of the bridging carbon atoms in α positions, which by themselves account for 79% of the correlation energy of the system (see Figure 3c).

Even Oligomers. We show in Figure 4 plots of the symmetry-unique spin-coupled orbitals of the two central rings in sexithiophene. Orbitals ϕ_1 and ϕ_2 again represent the (deformed) lone pair of sulfur: they are very similar to the corresponding orbitals determined for the odd oligomers. Orbitals ϕ_3 and ϕ_4 are localized on the α carbon atoms of the same ring. Orbital ϕ_3, localized on the central α carbon directly connected to the other correlated ring, shows deformations toward the corresponding central α carbon of the adjacent ring and toward the β carbon atom of the same ring. Orbital ϕ_4, localized on the peripheral α carbon atom connected to the “embedding” system, is instead similar to the corresponding orbital obtained for the odd oligomers, showing deformations toward the β carbon atoms of the same ring. Orbitals ϕ_5 and

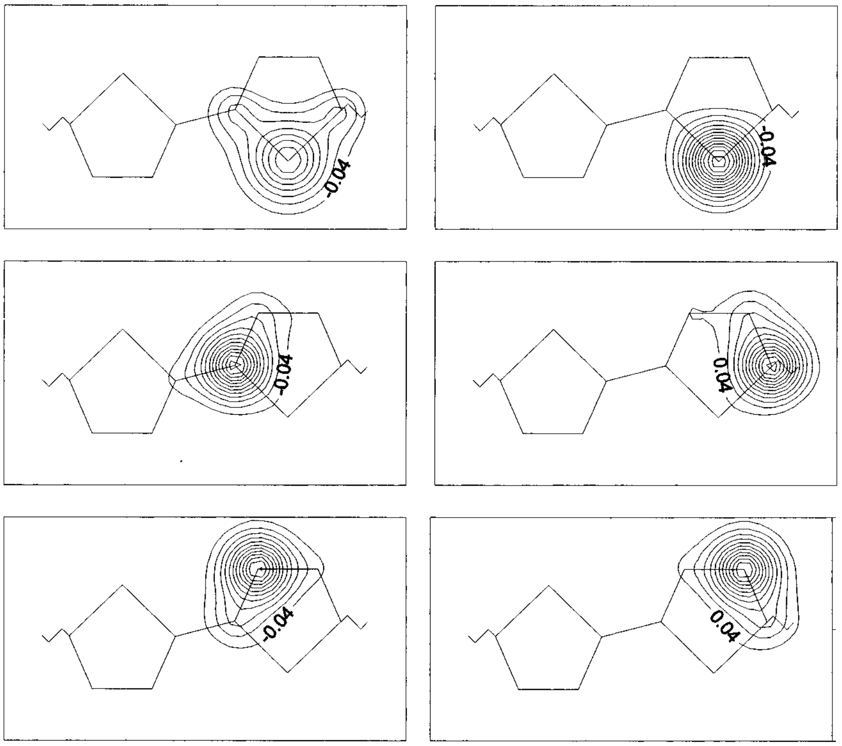
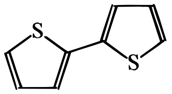


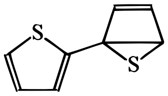
Figure 4. Plots of the symmetry-unique SC orbitals of the central rings of the hexamer.

ϕ_6, localized on the β carbon atoms, are very similar to the corresponding orbitals of the odd oligomers, independent of their central or peripheral position.

The analysis of the spin couplings shows that the perfect pairing (I) once more dominates the spin-coupled wave function, recovering 93.0% of the spin-coupled energy and that also the "Dewar" pairings (II and III) do not have negligible weights; together with the perfect pairing coupling, they account for 98.5% of the total spin-coupled energy.



(I)



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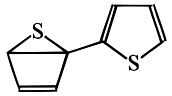

(III)

An analysis of the similarity of the corresponding orbitals of different oligomers gave results analogous to those obtained in the case of the odd oligomers. Again, the overlaps between corresponding orbitals of different subsystems are not a reliable and sufficiently sensitive index. The transferability of the orbitals is not guaranteed when embedding effects are not properly taken into account.

When computing the spin-coupled energy of the tetramer using the orbitals of the dimer, i.e., a "2 in 4" system, we recover 83% of the energy; this already acceptable result improves very satisfactorily when considering the "4 in 6" system, where 99% of the energy is obtained. Once more, the substitution of selected sets of spin-coupled orbitals reveals that the poor energy of the 2 in 4 system is mainly due to the quality of the orbitals of the peripheral α carbon atoms, see Figure 5; the use of the correct orbitals on these carbon atoms is by itself responsible for improving the description of the 2 in 4 system from 83% to 96% (Figure 5c). This also explains why the orbitals of the dimer reproduce 83% of the energy of the tetramer, while those of the monomer reproduce only 63% of that of the trimer (Figures 3a and 5a): in the first case there are ten "good orbitals" out of a total of twelve, to be compared with only four "good orbitals" out of a total of six in the trimer, confirming that the errors in the orbitals are concentrated on the peripheral α carbon atoms.

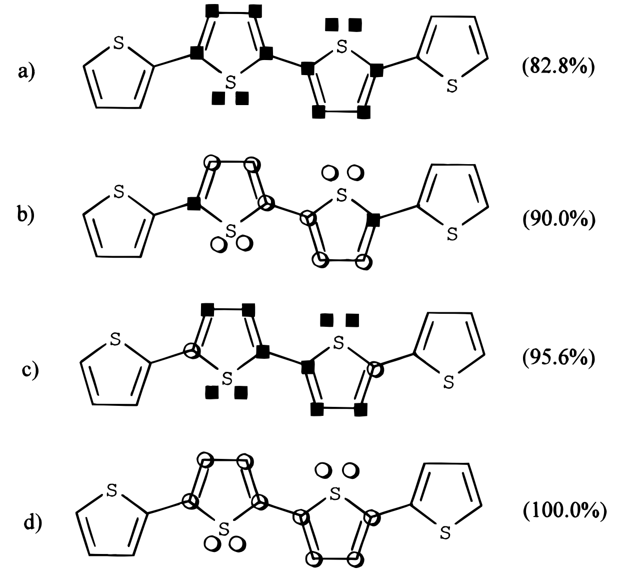

Figure 5. Schematic representation of the transferability of the orbitals from the dimer to the tetramer. The SC energy is computed for the tetramer, using two different sets of orbitals: the solid squares represent SC orbitals optimized for the dimer, the empty circles the SC orbitals optimized for the tetramer. In parentheses we give the percentage of the SC correlation energy of the tetramer (case d).

Separate Role of the Sulfur and Carbon Atoms. By performing separate spin-coupled calculations on sulfur or carbon electrons only, we investigated the extent to which these contributions can be considered additive. We tested this on the 2-, 4-, and 6-electron systems represented by the sulfur lone pairs of 1, 2, and 3 rings, embedded in systems of increasing size. In a similar way, by means of 4-, 8-, and 12-electron spin-coupled calculations, we studied the additivity of the contributions of the carbon electrons of 1, 2, and 3 rings, variously

TABLE 2: Values of ϵ_{SC}, ϵ', and ϵ''[a]

case	n_R	n_C	n_S	ϵ_{SC}	ϵ'	$100 \times \epsilon'/\epsilon_{SC}$	ϵ''	$100 \times \epsilon''/\epsilon_{SC}$
a	1	2	1	−56.142	−51.104	91.0	−49.721	88.6
b	2	4	0	−97.681	−92.538	94.7	−89.770	91.9
c	2	4	2	−110.968	−102.208	92.1	−99.442	89.6
d	3	2	0	−44.885	−46.269	103.1	−44.885	100[b]
e	3	2	1	−50.982	−51.104	100.2	−49.721	97.5
f	4	4	0	−92.538	−92.538	100[b]	−89.770	97.0
g	4	4	2	−105.137	−102.208	97.2	−99.442	94.6
h	5	2	1	−50.551	−51.104	101.1	−49.721	98.4
i	5	6	0	−140.657	−138.807	98.7	−134.655	95.7
j	6	4	0	−92.117	−92.538	100.5	−89.770	97.5
k	6	4	2	−104.709	−102.208	97.6	−99.442	95.0

[a] ϵ_{SC} represents the ab initio SC energy; ϵ' is estimated with eq 5, parameters determined from the tetramer; and ϵ'' is estimated with eq 5, parameters determined from the trimer. See text for details. The energy quantities are correlation energies in millihartree. [b] These values refer to calculations from which the parameters were derived.

embedded. From comparisons of spin-coupled energies obtained correlating the carbon and the sulfur electrons separately or together we found that the contributions of the individual subsystems add to give the 97% of the total spin-coupled correlation energy: in *all* the cases considered, the carbon electrons account for about 88% and the lone pairs of sulfur for about 9%. This clearly indicates that the greatest contribution to nondynamical correlation effects arise from the π system of the carbon atoms and that intergroup correlation between carbon and sulfur subsystems can be considered negligible. All of this seems to suggest that the role of the sulfur atoms is mostly that of introducing inductive effects rather than that of making chemically active contributions to the electronic structure of polythiophenes.

Transferability of the Spin-Coupled Orbitals. From the observed additivity of the correlation energies of the carbon and sulfur π electrons, we now propose a simple expression to predict, to a good approximation, the π electron spin-coupled correlation energy ϵ of a generic oligomer. We suggest the expression:

$$\epsilon = n_C\epsilon_C + n_S\epsilon_S \tag{5}$$

where n_C is the number of π C−C bonds and n_S the number of sulfur lone pairs in the correlated central rings; ϵ_C and ϵ_S are parameters representing the correlation energy of a single π C−C bond and of the sulfur lone pair, respectively. We have evaluated two sets of values for these parameters by considering calculations performed either on the trimer or on the tetramer.

By means of eq 5, we have estimated the correlation energy for systems constituted by different numbers of rings n_R, for which full spin-coupled results were available. In Table 2 we report these various estimates together with the correlation energy, ϵ_{SC}, computed at the spin-coupled level. The agreement is always in the range of 5%, with the obvious exceptions of the monomer and of the dimer (cases a and c in Table 2), due to the lack of embedding effects included at the spin-coupled level. The better results obtained using the parameters deduced from the tetramer (ϵ' in Table 2) indicate the importance of explicitly correlating more than a single ring. To check this important point further, we also studied the case where we have explicitly correlated the π C−C bonds of more than two rings, concentrating on the case of the three central rings of the pentamer. This final result (case i in Table 2) makes us confident that resonance effects are described sufficiently well by explicitly correlating only the two central rings of even oligomers.

From all of this, the assumption of additivity of the correlation energy contributions turns out to be entirely reasonable. It indicates that the direction to take when extending the size of the explicitly correlated system could be that of transferring the spin-coupled orbitals from properly chosen smaller systems.

TABLE 3: Energy Values Obtained with SCVB Wave Functions Including Single and Double Excitations for 1−6 Rings (6-31G basis set)[a]

number of rings	E_{SCVB} (au) no virtuals	E_{SCVB} (au) with virtuals	energy recovered by the occupied orbitals (%)
1	−551.243 637	−551.245 793	96.30
2	−1101.336 474	−1101.339 469	97.33
3	−1651.318 922	−1651.320 859	96.34
4	−2201.411 988	−2201.414 945	97.22
5	−2751.399 843	−2751.401 703	96.45
6	−3301.492 894	−3301.495 852	97.21

[a] The percentage recovered by including only the occupied orbitals is also reported. For the odd-ring systems the full spin space is considered, and for the even ones only perfect pairing and the two Dewar pairings are included.

SCVB Calculations. In order to verify the importance of also including the spin-coupled *virtual* orbitals to describe the electronic structure of the oligomers, we have performed some selected SCVB calculations. We report in Table 3 the SCVB energy values obtained by including single and double excitations into the first virtual orbital in each stack. For comparison, we also show the energy of the corresponding calculation without virtual orbitals. For the odd-ring systems (six valence π electrons) all of the spin space was included in the VB calculation. For the even-ring systems (twelve valence π electrons) we limited the spin space so as to reduce the dimension of the problem. On the basis of the analysis of the importance of the spin pairings in the spin-coupled wave function, we feel confident that the three spin structures corresponding to perfect pairing and to Dewar pairings can adequately describe the full spin space. Inspection of Table 3 shows that the spin-coupled wave function by itself always contributes more than 96% of the total SCVB energy. The same results are obtained for the 1 in 3, 2 in 4, 3 in 5, and 4 in 6 systems. This emphasizes that the spin-coupled orbitals provide a very good description of the ground state and confirms our previous considerations concerning the treatment of embedding effects, extending their validity also to virtual orbitals. This is expected to be of great importance in the development of a proper physical model of the transport properties of these systems.

It is interesting to note that the "quinoid" spin pairing, with double bonds between the β carbon atoms within a ring and between the α carbon atoms across two rings, is always negligible in the neutral oligomers considered. Its importance increases in the first excited state, and in some cases it becomes the predominant spin pairing.

The applicability of the SCVB wave function to the study of charge transfer processes was probed by a preliminary analysis on the larger oligomers, where the ionic structures were included either with or without the single excitations. Their importance in describing the ground state is indeed minimal, but a better description of the first excited state is gained, i.e., we calculate a narrower band gap. However, by applying an electric field along the chain, the weight of the ionic structures in the ground state becomes significant, suggesting that our approach could really be applied to the electric conductivity of the undoped oligomers.[20]

V. Conclusions

"There remain real challenges in extracting insight and not merely high quality numbers from electronic structure calculations".[32] In the spirit of this concluding sentence of a recent review work, we took advantage of the localized picture provided by the spin-coupled method to describe the chemical nature of the bonds in thiophene oligomers and to predict the electronic structure of the polymer. The valence π system of either one or two central rings of the oligomers was correlated at the spin-coupled level, and the effect of lateral rings on the correlated electrons was systematically analyzed. Our results strongly support the importance of "embedding" the explicitly correlated thiophene rings in a larger system and indicate that the inclusion of just the nearest neighbors is adequate to describe these effects; further addition of lateral rings does not cause significant changes to the electronic structure of the correlated units.

The role of the sulfur atoms in the chemistry of oligothiophenes was also investigated. From a comparison between all π electron calculations and separate calculations only on sulfur or carbon electrons, a near additive contribution of the two-electron systems was found, confirming the key role of the inductive effect of the sulfur atoms on the C−C backbone of the polythiophene.

We analyzed the possibility of defining the subsystem from which to extract the approximate spin-coupled orbitals of the polymer. From energy considerations, the orbitals of the tetramer turned out to be the most appropriate candidates for this job; they reproduce well the spin-coupled energy of the larger systems also when we explicitly correlated the π C−C bonds of three central rings. This also ensures that our procedure of including in the core also the valence π electrons of the embedding system does not prevent the transmission of the actual chemical and physical interactions on the explicitly correlated subsystem.

Finally, the possibility of charge transfer within a single oligomer was described in terms of the SCVB wave functions of the individual molecules of the oligomer involving excited and ionic structures. The importance of this analysis is to be considered as a preliminary approach for describing the electric and associated optical properties of pure and doped polythiophene, which of course represent the most appealing subject of research for this polymer. As anticipated in the Introduction, the most suitable approach in this case is likely to be a method similar to that of Davydov's treatment of the motion of excitons in molecular crystals.[20] This will be the subject of further work.

References and Notes

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