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MOLECULAR ORBITAL TREATMENT OF THE CONFORMATIONS OF COMPOSITE MOLECULES†

PHENYLTHIOPHENES

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Abstract—A correlative study of the theoretical determination of the conformation of composite molecules is given. Results of EH, M-I-M and CNDO/2 treatments are compared for the model composite systems; 2- and 3-phenylthiophenes. The systematic failure of the EH method reveals its inadequacy for conformational analysis of composite molecules. The transition energies, oscillator strengths and dipole moments of the two isomers, as calculated by the CNDO method, agree satisfactorily with experiment and confirm a planar equilibrium conformation for the studied composite molecules. The total charge distribution calculated by the CNDO method shows an appreciable σ-charge contribution and a comparatively small charge-transfer contribution. The formal σ-charges on the atoms of the two isomers are shown to be polarized in a direction opposed to that of the π-polarization. The molecular orbitals of the two isomers are found to possess similar nodal properties which indicates that the extent of cross conjugation in the 3-phenyl isomer is very limited.

The conformations and the geometrical parameters of many composite molecules have not yet been experimentally determined. Even if they had, apparant discrepancies exist between the results determined by NMR and X-ray spectra.[1,2]

The inadequacy of the resonance theory in predicting the geometries and electron distributions of composite molecules has been reported.[3,4] The problem becomes more complicated when considering linear and cross conjugation in such molecules.[5] A variety of molecular orbital approaches[6] were used to predict the molecular structure and conformations of composite molecules, yet no common agreement is reached.

The aim of the present paper is to introduce, in a correlative study, a fairly complete viewpoint regarding the structural conformation of composite molecules. Different molecular orbital treatments are compared for model compounds. In spite of their chemical and biological importance, isomeric 2- and 3-phenylthiophenes are selected as model compounds for two reasons. First, the constituting subsystems are extensively studied and their structures are in no doubt. Second, they are differentiated into linear (2-phenylthiophene) and cross (3-phenylthiophene) conjugated molecules.

Method of calculation

Since it is impractical to carry out *ab nitio* calculations on such large molecules, then the choice of the semi-empirical quantum mechanical method should be in such a way that the approximations introduced should not affect the primary physical forces determining the structure. This condition is satisfied within the CNDO/2 framework which is at the limit of sophistication that is practical for doing calculations on such large molecules.

CNDO/2 Formalism. The original CNDO parameterization[7,8] is basically retained in this work. However, the modifications suggested by Del Bene and Jaffe[9] which proved to be more successful for calculation of the energies and spectroscopic data were followed.

The core resonance integral β_{uv} is calculated by

$$\beta_{uv} = K/2(\beta_A + \beta_B)S_{uv} \quad (1)$$

where β_A and β_B are empirically determined resonance integrals for atoms A and B; S_{uv} is the overlap integral between orbitals u and v, and K is an empirical parameter equals 1 if u and v are σ-orbitals and equals[9] 0.585 if u and v are π-orbitals.

The singlet–singlet transition energies are calculated by the expression[10]

$$\Delta E = E_j - E_i - J_{ij} + 2K_{ij} \quad (2)$$

where E_j and E_i are the energies of the two orbitals between which the electronic transition occurs, J_{ij} and K_{ij} are the molecular coulomb and exchange integrals.

Molecule-in-molecule formalism. This method is included here for comparison with the all-valence electron method used. The M-I-M method classifies excited electronic states of a composite molecule into (a) "locally excited" states on each subsystem and (b) "charge transfer" states, arise from the transfer of an electron from a bonding molecular orbital on one subsystem to an antibonding molecular orbital on the other.

Stabilization energy. The stabilization energy of a composite molecule is given by:

$$E = E_{RS} - (E_R + E_S) \quad (3)$$

where E_{RS}, E_R and E_S are the total energies of the composite molecule (RS) and its constituting subsystems (R) and (S) respectively. A similar equation is used to calculate the stabilization energy due to π-interactions only.

Isomeric phenylthiophenes. The equilibrium conformation of phenylthiophenes is determined by a delicate balance of both steric and conjugative effects. The experimental geometrical parameters of phenylthiophenes are not reported, yet using the standard geometrical parameters of both thiophene[13] and ben-

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zene,[14] the planar conformers of 2-phenylthiophene (1) and 3-phenylthiophene (2) do not show any steric hinderance due to the ortho–ortho hydrogens (Fig. 1). As a result, the planar conformers (1 and 2) are favoured by conjugative effects and would have lower energies. Extended Huckel calculations[15] showed that the planarity of these molecules is appreciabally distorted and the angle between the planes of the two rings amounts to 37°. Our previous study,[12] however, seriously contradicted this result.

RESULTS

Using the standard geometrical parameters of both benzene and thiophene, the energies of the two isomeric phenylthiophenes were minimized with respect to the bond length r_{A9}, between the two rings (atom A is number 2 or 7 in thiophene). The results obtained indicate that, in the planar conformers, a bond length of 1.44 and 1.45 A represent the equilibrium distance between the two moities, benzene and thiophene, for 2- and 3-phenylthiophenes respectively. For the perpendicular conformers the energy is not sensitive to the change of r_{A9} indicating a diminished interaction between the two rings. Energy is a minimum for the planar conformer and for the two isomers showed a high dependance on the angle of twist of the two nuclei. Results are given in Table 1.

Transition energies were calculated using eqn (2) and are given in Table 2 together with those calculated considering π-interactions only (M-I-M method).

DISCUSSION

Results obtained by the CNDO/2 calculations are in good agreement with experiment, indicating that σ-electrons have a considerable effect on the electronic stabilization of the composite molecules, 2- and 3-phenylthiophenes. The charge distribution among atoms of the two moieties (Table 3) indicates the following:

(1) There is a little "charge-transfer" contribution to the ground states of the two isomers; 4.3% and 2.7% for the 2- and the 3-phenylthiophenes respectively. In both cases the direction of charge migration is from benzene to thiophene. This goes with the fact that the energies of the highest occupied orbitals of benzene and thiophene have very comparable values;[16] 9.25 and 9.1 eV respectively. Electron affinity values favour the donation to the thiophene vacant orbitals.

(2) The σ-bond framework of the phenylthiophenes is polarized to a great extent. The formal σ-charges on the atoms follow the electronegativity order S > C. On the other hand, the π-charges do not reflect this electronegativity order (q_π on S is less than that on C). The π-polarization may be opposing the σ-polarization in these systems. The contribution of the σ-charges to the total charge distribution is appreciable. A similar behavior has been reported for substituted oxazoles.[17]

In conclusion, stabilization in the planar conformers of the two isomers results from π and σ-orbital interactions as well as from "charge-transfer" contribution.

In the perpendicular conformers, the π- as well as the "charge-transfer" interactions are zero and the only interaction will be between the π-system of one ring and the σ^*-orbitals of the other. Such interactions are weak and the electronic spectra of the composite molecules are expected to be the additive spectra of the two constituting subsystems if the perpendicular conformers contribute significantly to the states of the composite molecules. Experimentally (Fig. 2) the spectra of the composite molecules, phenylthiophenes, differ significantly from those of their subsystems.

Agreement between the calculated (1.12 D) and the experimental[18] (1.04 D) dipole moments of 2-phenylthiophene excellently confirms the planar conformer for this molecule. The experimental dipole moment of 3-phenylthiophene has not been reported, yet a value of 1.8 D, as our calculations give, is reasonable as compared with the value for the 2-phenyl isomer. Thiophene has a dipole moment[18] of 0.52 D, conjugation with a benzene ring increases its dipole moment. Perpendicular conformers, with diminished interaction between thiophene and benzene nuclei, can not account for such an increase.

The M-I-M method predicts that the planar conformers of the 2- and 3-phenylthiophenes are the equilibrium ones. On the other hand, the extended Huckel treatment[15] predicts, for the same isomers, nonplanar equilibrium conformers with a twisting angle of 37°. These conformations give −29.311 and −29.313 a.u. as the total energies for 2- and 3-phenylthiophenes respectively; any of these values is even lower than the sum of the total energies of benzene and thiophene (−41.2979 a.u.). The dipole moments calculated using the EHT are in very poor agreement with the experimental ones. Essentially, the results of EHT reflects the absence of any interaction

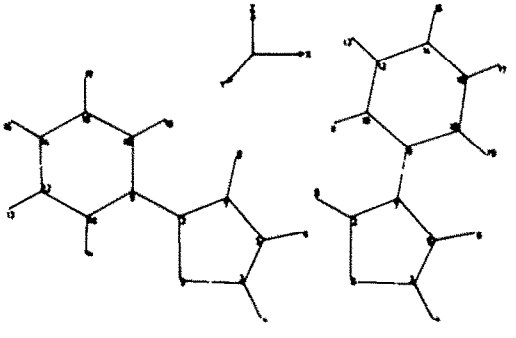


Fig. 1. Numbering system and coordinate system for phenylthiophenes.

Table 1. Equilibrium conformation parameters[a] for 2- and 3-phenylthiophenes

Compound	HOMO[b]	LEMO[c]	Total $E_{\sigma,\pi}$ CNDO	Energy E_π MIM	Binding energy	μD Calc.	μD Exp.
2-Phenylthiophene	−0.436	0.0612	−87.52	−14.14	−9.995	1.12	1.04
3-Phenylthiophene	−0.402	0.0684	−87.50	−13.99	−9.955	1.8	—

[a] Energies are in Hartree.
[b] Highest occupied molecular orbital.
[c] lowest empty molecular orbital.

Table 2. Singlet–singlet transition energies (eV) and stabilization energies (Hartree) of 2- and 3-phenylthiophenes

Compound	First $\pi \rightarrow \pi^*$	f	Second $\pi \rightarrow \pi^*$	f	Stabilization energy
2-Phenylthiophene					
Calc. (CNDO)	4.33	0.6	4.58	0.22	−46.223
Calc. (MIM)	4.66	0.4	4.73	0.06	−3.596
Calc. (EHT)	—	—	—	—	11.987
abs.	4.4	0.4	4.63	0.19	—
3-Phenylthiophene					
Calc. (CNDO)	4.4	0.1	4.65	0.31	−46.203
Calc. (MIM)	4.79	0.02	4.97	0.1	−3.455
Calc. (EHT)	—	—	—	—	11.985
abs.	4.51	0.07	4.77	0.24	—

Table 3. Charge distribution in phenylthiophenes†

Atom	2-Phenylthiophene q_σ	2-Phenylthiophene q_π	2-Phenylthiophene q_{total}	3-Phenylthiophene q_σ	3-Phenylthiophene q_π	3-Phenylthiophene q_{total}
S	−0.0688	−0.0224	−0.0912	−0.0921	0.0123	−0.0798
C-2	0.0173	−0.0371	−0.0198	0.0066	−0.0594	−0.0527
C-3	−0.0043	−0.0357	−0.04	−0.0157	−0.0174	−0.0331
C-5	0.0112	0.0287	0.0399	0.0116	0.0109	0.0225
C-7	0.0159	−0.0013	0.0146	0.0219	0.0449	0.0668
C-9	0.0243	0.0242	0.0485	0.014	0.0112	0.0252
C-10	−0.0043	−0.0164	−0.0207	−0.0107	−0.0087	−0.0194
C-11	−0.0145	0.0107	−0.0038	−0.0127	0.0069	−0.0058
C-14	−0.0061	−0.0088	−0.0149	−0.0094	−0.0007	−0.0101
C-16	−0.0136	0.0102	−0.0034	−0.0132	0.0071	−0.0061
C-18	−0.0057	−0.0204	−0.0261	−0.0101	−0.0073	−0.0174
		$P_{2-9} = 0.2978$			$P_{7-9} = 0.2907$	

†See the numbering system.
P_{A-B} is the mobil-bond order between atoms A and B.

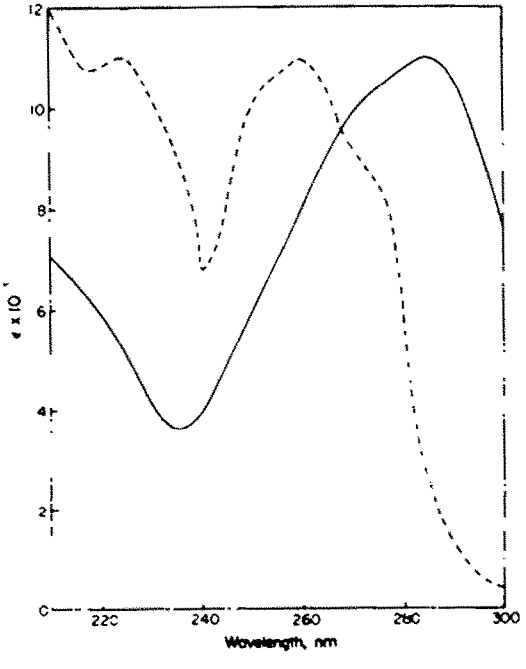
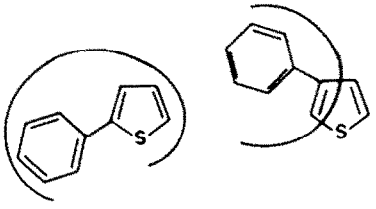


Fig. 2. Electronic absorption spectra of 2-phenylthiophene (—) and 3-phenylthiophene in ethanol (----).

between the two subsystems of a composite molecules.

Cross and linear conjugation. Classically, the two isomeric phenylthiophenes are differentiated into cross and linear conjugated systems



If this classification is a predominent factor in determining the physical properties of the molecules one would expect the spectrum of the 3-phenyl isomer to be similar to that of styrene and to differ significantly from that of the 2-phenyl isomer. Fig. 2 shows that the spectra of the two isomers are very much similar. Hence, the extent of conjugation in both isomers is almost equal. The lowest six π-molecular orbitals of the two isomers are represented in Fig. 3. The nodal properties of the molecular orbitals of the two isomers are very much similar indicating that in both isomers, the degree of conjugation is the same.

Extension to other composite systems. The present results provide a good framework to handle similar

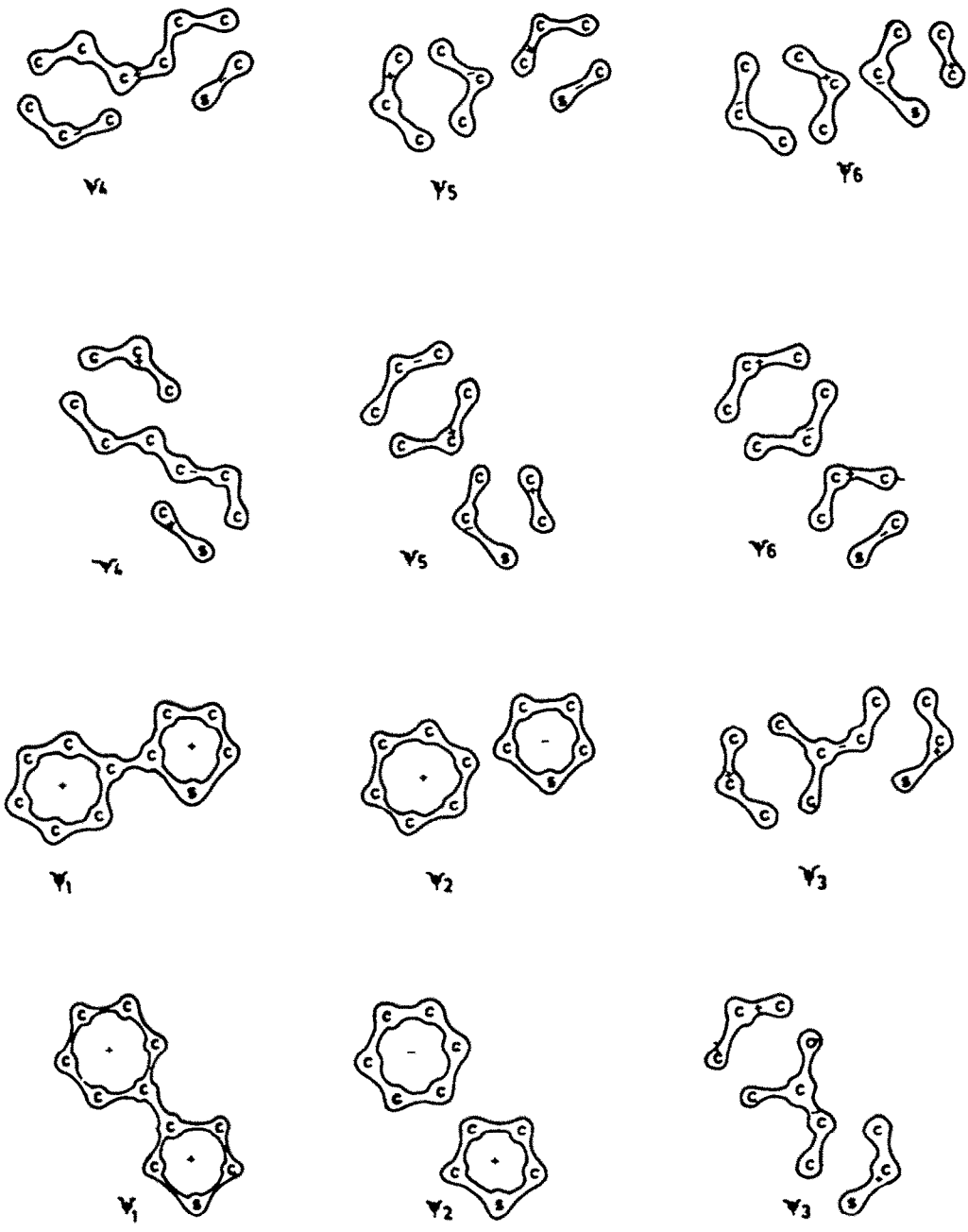


Fig. 3. Nodal properties of the lowest six molecular orbitals of phenylthiophenes.

composite molecules, phenylfurans for example. The difference between the ionization potential of benzene (9.25 eV) and that of furan[16] (8.89 eV) is significant and one would expect an appreciable "charge-transfer" contribution to the stabilization of such compounds. On this basis, phenylfurans must be more stabilized than the corresponding thiophene analogues. Preliminary INDO calculations on phenylfurans reveal greater stability for the planar conformers and give a relatively greater value for the barrier of rotation from the planar equilibrium conformation (14.74 eV). The total energies of the 2-phenyl (−91.261 a.u.) and 3-phenylfurans (−91.08 a.u.) as given by the CNDO/2 calculations are greater than the corresponding energies of phenylthiophenes due to the increased stabilization via "charge-transfer" interactions.

CONCLUSIONS

Many of the calculated parameters, namely (i) transition energies, (ii) dipole moments and (iii) the similarity of the nodal properties of the MO's of 2- and 3-phenylthiophene agree fairly well with their experimental values and lead one to conclude:

(1) neglecting σ- and "charge-transfer" interactions in composite molecules causes serious errors in calculating their structure and their electronic spectra.

(2) all-valence electrons molecular orbital calculations

carried out with the CNDO or INDO approximations of atomic and molecular integrals are quite capable of accommodating structural conformation problems in composite molecules.

(3) differentiation of composite systems, as those studied, into cross and linear conjugated is not adequate.

(4) the extended Hückel method of calculation is inadequate for studying the geometry of composite molecules.

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