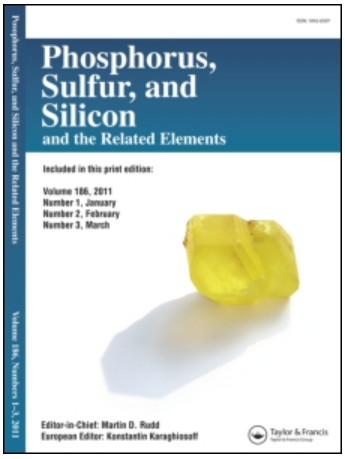

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ELECTRONIC STRUCTURE OF BENZO(b)THIOPHENE

C. Guimon[a]; M. F. Guimon[a]; G. Pfister-guillouzo[a]; P. Geneste[b]; J. L. Olive[b]; S. N. Ung[b]
[a] Laboratoire de Chimie, Organique Physique I.U.R.S., Pau [b] Laboratoire de Chimie, Organique Physique Appliquée E.N.S.C.M., Montpellier Cedex

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ELECTRONIC STRUCTURE OF BENZO(b)THIOPHENE

C. GUIMON, M. F. GUIMON and G. PFISTER-GUILLOUZO

Laboratoire de Chimie Organique Physique I.U.R.S., Avenue Philippon, 64000 Pau

P. GENESTE, J. L. OLIVE and S. N. UNG

Laboratoire de Chimie Organique Physique Appliquée E.N.S.C.M., 8, Rue de l'Ecole Normale—34075 Montpellier Cedex

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In this paper we examine the electronic structure of benzo(b)thiophene and some of its substituted derivatives. The study is carried out using the data of photoelectron spectroscopy in conjunction with semi-empirical calculations (EHT, CNDO/S). The results thus obtained and analysed with a perturbational scheme allow a quite satisfying qualitative correlation between the nucleophilic reactivity of those compounds and the energies (and localization) of frontier orbitals.

INTRODUCTION

The study of the electronic structure heteroaromatic five-membered rings  has been the subject of several systematic works in recent years.[2–14] However, the data gathered on their benzologs remain limited in spite of the fact that they are basic components of several natural products of biological interest.

In this paper we will discuss the characteristics of benzo(b)thiophene using the data of photoelectron spectroscopy together with descriptions of molecular orbitals obtained from semi-empirical calculations (EHT, CNDO/S).[15–16] We use for the comparative study of annelation effects a perturbational scheme. This PMO treatment seems to be well suited because there are no subtle effects such as inductive[17] and distortion effects: the geometric structure of the benzo group being approximately the same for all compounds.

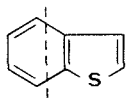
CALCULATION METHODS

In order to rationalize an electronic structure, one must determine the interactions between orbitals localized on different parts of the molecule, that is to say, to estimate the importance of the ϕ_j localized orbitals in the construction of the Ψ_i molecular orbitals. To this end, we have used an EHT calculation (Extended Hückel Theory)[15] for the entire molecule (thus allowing us to compose the Ψ_i molecular orbitals from the basis of the atomic orbitals χ_j: $\Psi_i = \sum_j a_{ij}\chi_j$) and for each subunit ($\phi_i = \sum_j b_{ij}\chi_j$). This calculation allowed us to write the Ψ_i molecular orbitals in terms of the ϕ_j orbitals of the different subunits: $\Psi_i = \sum_j c_{ij}\phi_j$ (c_{ij} coefficients being simply deduced from a_{ij} and b_{ij} coefficients). We chose that technique because, in addition to its simplicity, it is a one-electron method which easily lends itself to a perturbation treatment.

In addition we give the results of CNDO/S calculation.[16a] This method is one of the most adaptable semi-empirical methods for the description of molecular orbitals associated with the ionization potentials measured by photoelectron spectroscopy. In this calculation, we took into account the sulphur *d* orbitals according to a previously presented parametrization.[16b]

BENZOTHIOPHENE

We have considered the benzo(b)thiophene molecule as the juxtaposition of two subunits: *cis*-butadiene (Φ) and thiophene (ϕ)



In Figure 1 we recall the HOMO's (Φ and ϕ) and LUMO's (Φ^* and ϕ^*) of the two subunits, as well as their symmetries.

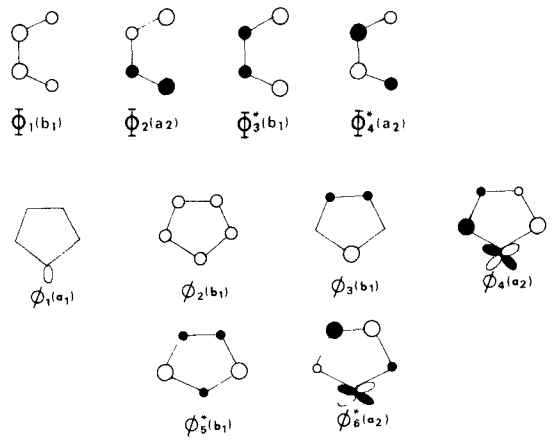


FIGURE 1 HOMO's (Φ and ϕ) and LUMO's (Φ^* and ϕ^*) of *cis*-butadiene (Φ) and thiophene (ϕ).

Table I shows the main coefficients involved in the development of the π Ψ_i HOMO's of benzo(b)-thiophene (Figure 2) on the basis of ϕ_j and Φ_k molecular orbitals of both moieties (EHT calculation).

In Table II the coefficients involved in the development of those orbitals are given, but on the basis of the χ_j atomic orbitals (CNDO/S and EHT calculations).

The orbital mixing of a single subunit with orthogonal orbitals before the approach of the other subunit can also be estimated through perturbation theory.[20–22] In fact, at the approach of two A and B subunits a Φ orbital of A may interact with two or more ϕ_i and ϕ_j orbitals of B. The molecular orbital Ψ is then given to a second-order approximation by:

$$\Psi = \phi_i + \frac{\langle \Phi/H/\phi_i \rangle}{\varepsilon_\Phi - \varepsilon_{\phi_i}} \Phi + \frac{\langle \Phi/H/\phi_i \rangle \langle \Phi/H/\phi_j \rangle}{(\varepsilon_\Phi - \varepsilon_{\phi_i})(\varepsilon_{\phi_i} - \varepsilon_{\phi_j})} \phi_j \quad (1)$$

This description of the benzo(b)thiophene HOMO's is confirmed by photoelectron spectroscopic data (Table III). Thus, if we associate the eigen values ε_i of the molecular orbitals with the first ionization potentials through Koopman's theorem,[23] the shifts of the ionization potentials due to several substitutions (Table III) correspond perfectly to the localization of the molecular orbitals on the different atoms of the molecule (Table II). Thus, substitution in either the α or β position relative to the sulphur similarly shifts the first potential. On the contrary, methylation at α destabilizes the Ψ_4 orbital (associated with the second ionization potential) more than methylation at β, while the Ψ_3 orbital (associated with the third ionization potential) shows exactly the opposite behaviour.

Before examining more thoroughly the experimental data, we must add a few remarks on the theoretical results. The π HOMO of benzo(b)thiophene indicates important mixing of semi-localized orbitals, specifically the ϕ_3 and ϕ_4 thiophene orbitals (note that the sign of the coefficients of Table I confirms the mixing rule of Fukui *et al.*[24]). Due to the energetic proximity of the ϕ_3 and ϕ_4 molecular orbitals, this mixing (Figure 2) indicates a more complex situation described than by Epiotis *et al.*[3] who only mentioned the most important interactions, i.e. the interactions between the Φ_1 and ϕ_4 molecular orbitals on the one hand and the Φ_2 and ϕ_3 on the other (corresponding to the dashed line ---- in Figure 2). Epiotis's simple model seems to be correct only if the ϕ_3 and ϕ_4 orbitals are clearly energetically differentiated, i.e. when the third term of Eq. (1) becomes negligible, which is the case for pyrrole (1 eV spacing compared to 0.6 eV in thiophene) and above all for furan (1.43 eV). In the last case, the most important participation in the Ψ_5

TABLE I

Main c_{ij} and c_{ik} coefficients involved in the development of the highest π molecular orbitals of benzo(b)thiophene (Ψ) on the basis of the molecular orbitals of the subunits (ϕ for the thiophene, Φ for the *cis*-butadiene) from EHT calculations

$$\Psi_i = \sum_j c_{ij}\phi_j + \sum_k c_{ik}\Phi_k$$

	ϕ_2	ϕ_3	ϕ_4	ϕ_5^*	ϕ_6^*	Φ_1	Φ_2	Φ_3^*
Ψ_2	0.46	0.22	0.30			−0.79		
Ψ_3		−0.63	0.31	−0.11			0.60	
Ψ_4		0.40	0.72			0.47		−0.31
Ψ_5		−0.59	0.39	0.21	0.13		−0.67	

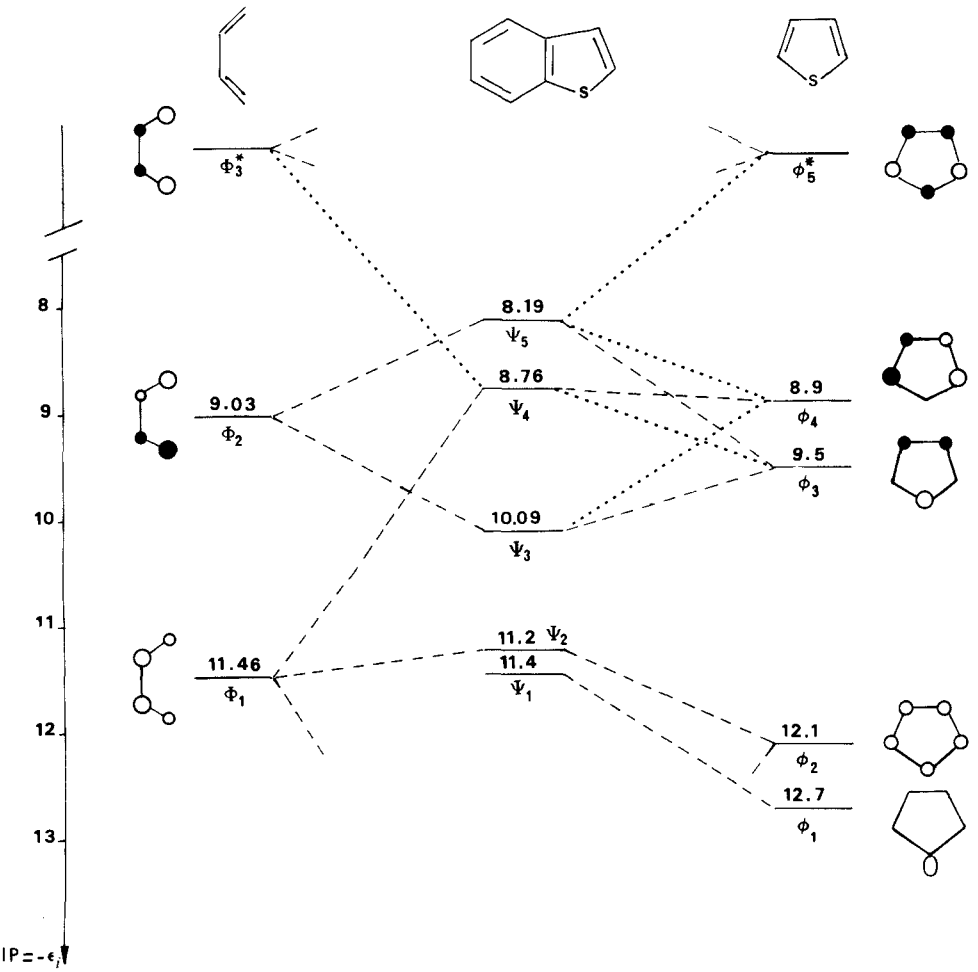


FIGURE 2 Major contributions of the molecular orbitals of the subunits at the HOMO's of benzo(b)thiophene (Table II). The reported values are the ionization potentials of butadiene,[11] benzo(b)thiophene (Table IV) and thiophene[5] (according to Koopman's theorem). In the perturbational scheme, the dashed lines ––– are associated with the term

$$\frac{\langle \Phi/H/\phi_i \rangle}{\varepsilon_\Phi - \varepsilon_{\phi i}}$$

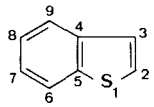
of Eq. (1) and the dotted lines .... are associated with the term

$$\frac{\langle \Phi/H/\phi_i \rangle \langle \Phi/H/\phi_j \rangle}{(\varepsilon_\Phi - \varepsilon_{\phi i})(\varepsilon_{\phi i} - \varepsilon_{\phi j})}.$$

HOMO comes from the ϕ_4 orbital, which reverses the order of electrophilic attack (preferential at the α position for benzo(b)furan and at β[25] for indole and benzo(b)thiophene). These results allow us to conclude that electrophilic substitution in these compounds is controlled by frontier orbitals.[26] In addition the spacing of ϕ_3 and ϕ_4 orbitals is more important for pyrrole than for thiophene and ϕ_4 participation in Ψ_5 is therefore less important for indole than for benzo(b)thiophene. Moreover, since the Φ_2 and ϕ_3 orbitals are energetically closer when the heteroatom is nitrogen (−9.03 eV for Φ_2 in butadiene, −9.10 eV for ϕ_3 in pyrrole and −9.50 eV for ϕ_3 in thiophene), their interaction is more important in indole, and its HOMO shows a major contribution of ϕ_3.[27] This implies that, for an electrophilic attack, the differentiation of the α and β centres must be more important for indole than for

TABLE II

ε_i eigen values and a_{ij} eigen vectors ($\times 100$) associated with the π HOMO's of benzo(b)thiophene obtained from EHT and CNDO/S calculations. The last column shows the corresponding ionization potentials according to Koopmans' theorem[23]

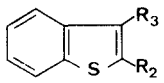


Coefficients $a_{ij} \times 100$ of $\Psi_i = \sum_j a_{ij}\chi_j$

Atom		1	2	3	4	5	6	7	8	9	ε_i (eV)	IP (eV)
Ψ_5	CNDO/S	−43	42	43	−21	−12	33	34	−7	−39	−9.62	8.19
	EHT	−51	27	42	−3	−3	37	28	−21	−39	−12.08	
Ψ_4	CNDO/S	46	28	−1	−35	−47	−21	28	46	12	−10.13	8.76
	EHT	28	36	0	−38	−40	−10	36	40	1	−12.58	
Ψ_3	CNDO/S	−49	14	35	32	−29	−42	−21	18	42	−11.68	10.09
	EHT	−33	16	38	34	−24	−38	−22	10	35	−13.26	
Ψ_2	CNDO/S	46	43	35	8	4	−25	−42	−41	−22	−13.44	11.20
	EHT	41	29	13	10	2	−23	−37	−39	−30	−14.10	

TABLE III

Adiabatic (IP_a) and vertical (IP_v) (eV) ionization potentials of benzo(b)thiophene and some substituted derivatives. The values between parenthesis correspond to the potentials associated to the substituents (σ and π lone pairs of halogens, σ lone pair of oxygen, π HOMO's of phenyl group and π orbital of ethylene group)



		1st		2nd	3rd	4th	5th
R_2	R_3	IP_a	IP_v	IP_v	IP_v	IP_v	IP_v
H	H	8.19	8.19	8.76	10.09	11.2	11.4
Me	H	7.96	8.08	8.5	9.88	10.95	11.25
H	Me	7.95	7.95	8.60	9.78	11.05	11.35
Br	H	8.19	8.35	8.74	10.17 (10.72, 10.90)	11.55	11.87
H	Br	8.19	8.35	8.90	9.85 (10.67, 11.06)	11.7	
Cl	H	8.31	8.50	8.84	10.24	11.06 (11.45)	
H	Cl	8.26	8.41	8.95	10.03 (11.35)	11.8	
Cl	Cl	8.35	8.50	8.95	10.20 (11.16, 11.58, 11.73, 12.6)		
Me, Me	H	7.65	7.80	8.22 (9.40)	9.90	11.3	11.3
$COCH_3$	H	8.40	8.55	8.92 (9.51)	10.22	11.25	11.65
H	$COCH_3$	8.30	8.45	8.90 (9.32)	10.10	11.3	11.6
C_6H_5	H	7.75	7.88	8.34 (9.3, 9.5)	9.96		
MO		π	π	$\pi\pi_\phi$ or $n_\sigma(o)$	$\pi n_\sigma(x)$ and $n_\pi(x)$	π	n_S

benzo(b)thiophene. This is in fact observed (Table IV).

The reactivity between these two compounds is thus essentially due to the mixing of semi-localized orbitals and not to the energetic spacing of both HOMO's (0.57 eV spacing for benzothiophene and 0.61 eV for indole). On the other hand, for benzofuran in which mixing is negligible, the faint differentiation of both the α and β centres[25] is due to the energetic proximity of both HOMO's (Table V).

In conclusion, we note that the energetic positions and the localization the HOMO's of these

TABLE IV

Compared reactivities of carbons 2 and 3 of thiophene, benzo(b)thiophene and indole[28]

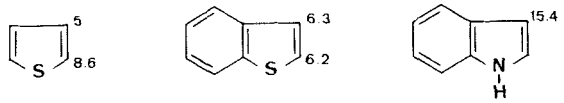
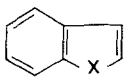


TABLE V

First vertical ionization potentials (eV) of indole, benzo(b)thiophene and benzo(b)furan



X			
NH[a]	7.87	8.48	9.89
S	8.19	8.76	10.09
O	8.58	8.95	10.55

[a] Ref. 9.

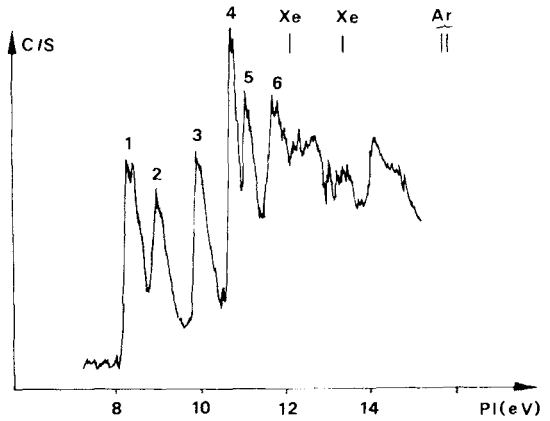


FIGURE 4 Photoelectron spectrum of 3-bromo benzo(b)-thiophene.

compounds are in perfect agreement with the reactivity of the different centres[25]: β(thiophene) ~ β(furan) < β(benzofuran) ~ α(benzothiophene) < β(benzothiophene) ~ α(benzofuran) ≪ α(thiophene) ≪ α(furan).

BENZO(b)THIOPHENE SUBSTITUTED IN POSITION 2 OR 3

Table III presents the values of the vertical ionization potentials (and the values of the first adiabatic potential) of some substituted derivatives of benzo(b)thiophene. Except for this compound and its 3-methyl derivative, with the first vertical potential equal to the adiabatic potential (0 ← 0 transition), the first vertical potential is a 1 ← 0 transition, with the vibrational frequency of ionized state between 950 and 1300 cm^{-1} ($\pm$ 50 cm^{-1}) (Figure 3 to 6).

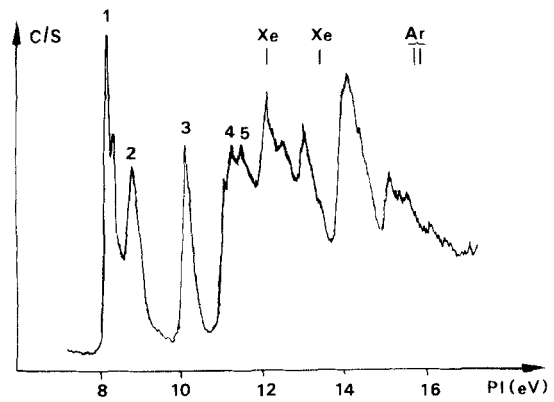


FIGURE 3 Photoelectron spectrum of benzo(b)thiophene.

Upon substitution the modifications of the electronic structure of a molecule are owing to both an inductive effect, provoking a polarization of molecular orbitals, and a conjugative effect which corresponds to a through-space interaction between the orbitals of the substituent and the molecule. These two effects may reinforce or work against each other. Consequently, the inductive influence of halogens induces a stabilization of HOMO's while the conjugative coupling between the π orbitals and the π halogen pair produces, on the contrary, a destabilization of the HOMO's of the unsubstituted molecule. Since chlorine is more electronegative than bromine, its inductive influence is more important, while the conjugative influence is weaker (the π pair of chlorine is more stable than bromine).

The shifts due to conjugative interactions depend not only on the spacing of the unperturbated orbitals but also on their overlap. Thus, according to the shape of the HOMO's of benzo(b)thiophene (Table

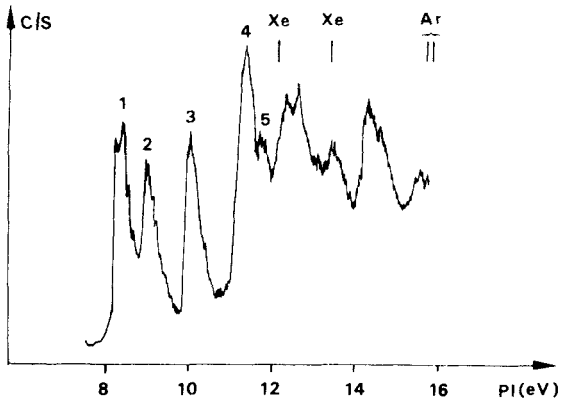


FIGURE 5 Photoelectron spectrum of 3-chloro benzo(b)-thiophene.

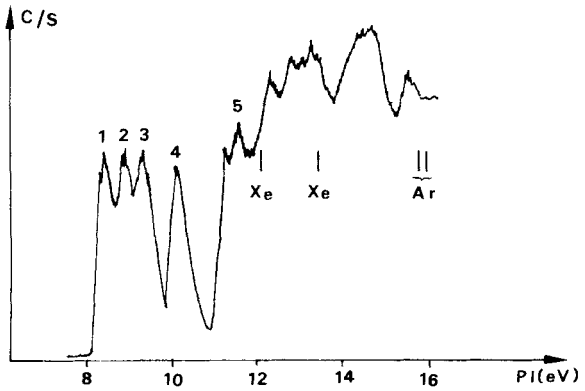


FIGURE 6 Photoelectron spectrum of 3-acetyl benzo(b)-thiophene.

II), the second band must be more sensitive to the destabilizing influence of an α-substituent, while the third band will be more sensitive to a β-substituent.

TABLE VI

Variations of the first ionization potentials ($IP_{non\text{-}subs.mol.} - IP_{subs.mol.}$) of benzo(b)thiophene with substitutions in α or β position of sulphur

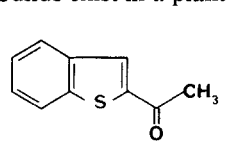
R_2	R_3	ΔIP_1	ΔIP_2	ΔIP_3
Me	H	0.23	0.25	0.21
H	Me	0.24	0.16	0.31
Br	H	0	0.02	−0.08
H	Br	0	−0.14	0.24
Cl	H	−0.12	−0.08	−0.15
H	Cl	−0.07	−0.19	0.06
Cl	Cl	−0.16	−0.19	−0.11
$CH{=}C(Me)_2$	H	0.54	0.54	0.19
COMe	H	−0.21	−0.16	−0.13
H	COMe	−0.11	−0.14	−0.01
C_6H_5	H	0.44	0.42	0.13

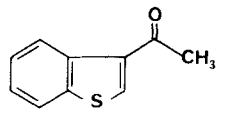
With bromine derivatives (Table III) the first ionization potential remains the same (the inductive and conjugative effects are equal) while the second and third potentials are shifted in the opposite direction. These shifts (Table VI) are in perfect agreement with the preceding remarks.

Although the inductive and conjugative effects of an isobutenyl[29] group act in the same direction as those of halogens, this is not so for the acetyl. Its inductive and conjugative influences tend to stabilize all the HOMO's of benzo(b)thiophene.[29]

In addition to the indications on electronic structures, photoelectron spectroscopy can give information on molecular conformation and in particular on the respective spacial positions of two conjugated systems[30,31] through the analysis of interactions between their molecular orbitals.

Table VII shows the ionization potentials ($-\varepsilon_i$) calculated from CNDO/S of the different conformers of 2-acetyl and 3-acetyl benzo(b)thiophene, as well as those of the unsubstituted molecule. The comparison of calculated and experimental shifts (Table VI) leads us to conclude that both compounds exist in a planar conformation.[32]





For 3-acetyl benzo(b)thiophene, the shift of the ionization potential associated for the n_σ lone pair of oxygen is consistent with *s-trans* conformation for the C=C and C=O double bonds.

As for the 1,3-diene[33] the conformational preference can be explained by an analysis of the interactions between the semilocalized orbitals on the unsubstituted molecule and the substituent. Indeed, the interaction between the doubly filled orbitals ϕ and Φ induces a ΔE destabilization of the entire system proportional to their mutual overlap $S_{\phi\Phi}$.

$$\Delta E = \frac{2S_{\phi\Phi} \mid S_{\phi\Phi}(E_\Phi^\circ + E_\phi^\circ) - 2H_{\phi\Phi} \mid}{1 - S_{\phi\Phi}}$$

In addition, it is obvious from Table II and Figure 7 that overlap is more important for *s-cis* forms than for *s-trans* forms. In the *s-cis* the overlap between the $\pi_{C=O}$ orbital and the HOMO's of benzo-(b)thiophene is always bonding whereas it is antibonding for some HOMO's in the *s-trans* forms (for Ψ_4 and Ψ_5 in particular).

Although we may conclude that acetyl and isobutenyl benzo(b)thiophene are planar, this is not the case for phenyl-2 benzo(b)thiophene.

TABLE VII

Calculated (CNDO/S) and experimental (eV) ionization potentials of benzo(b)thiophene and its 2-acetyl and 3-acetyl derivatives

Benzo(b) thiophene		2-Acetyl benzo(b) thiophene			3-Acetyl benzo(b) thiophene		
		IP_{calc}			IP_{calc}		
IP_{calc}	IP_{exp}	*trans*	*cis*	IP_{exp}	*trans*	*cis*	IP_{exp}
9.62	8.19	9.81	9.84	8.40	9.76	9.84	8.30
10.13	8.76	10.29	10.36	8.92	10.25	10.37	8.90
		10.97	10.94	9.51	10.69	10.92	9.32
11.68	10.09	11.87	11.90	10.22	11.69	11.85	10.10

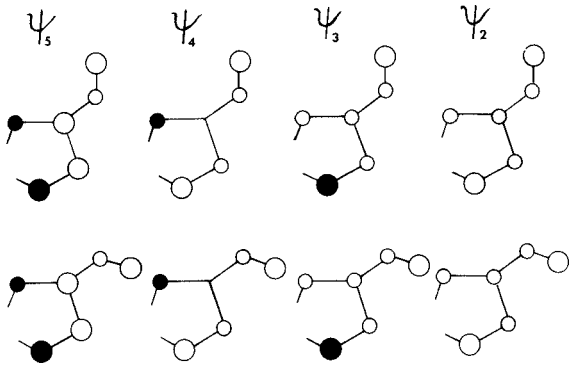


FIGURE 7 Interactions between π_{CO} orbital of 3-acetyl substituent and the π HOMO's of benzo(b)thiophene.

Planarity in 2-phenyl-benzo(b)thiophene would produce a more important destabilization of both HOMO's of benzo(b)thiophene for the phenyl compound ($\pi_\phi = -9.25$ eV) than for the derivative substituted by the isobutene moiety ($\pi_{C=C} = -9.45$ eV). Moreover, both degenerate HOMO's of benzene would undergo an important splitting. This is not the case since the HOMO of the phenyl derivative is more stable than the one for the isobutene derivative and the band associated with the HOMO's of the phenyl group only shows a small splitting of 0.2 eV. Thus, it seems that the phenyl group is not in the same plane as the heterocycle. However, the rotation must be much less than 90° since a 90° rotation would produce much smaller effects.

EXPERIMENTAL

The preparation of all compounds have previously been described,[34] with the exception of phenyl-2 benzothiophene[35] and (methyl-2 propenyl)-2 benzothiophene.[36]

In this study we used a Perkin Elmer PS 18 photoelectron spectrometer with a flowing helium discharge lampsource (He(I), 584 Å). The resolution was about 20 meV. The spectra were calibrated with the $^2P_{1/2}$ and $^2P_{3/2}$ doublet of xenon (12.127 and 13.427 eV) and argon (15.755 and 15.943 eV).

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