

## Theoretical Investigation of Electronic and Molecular Structures of Bithiopyranylidene and Related Conducting Complexes

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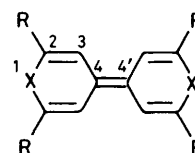
Electronic structures of bipyranlydene (BIPO) and bithiopyranylidene (BIPS) have been investigated by means of *ab initio* theoretical calculations. Evolution of the molecular structures of bithiopyranylidene and related compounds upon substitution and doping with electron acceptors (iodine, TCNQ) are explained on the basis of Molecular Orbital theory.

The concept of aromaticity is used almost pervasively to explain the electronic properties and behaviour of conducting charge-transfer complexes, and to design new compounds, with hopefully improved performance. In these attempted syntheses, classical aromatic molecules are often chosen as starting materials and two main strategies are then applied to enhance the electron donating and/or accepting character: the branching of groups on the molecules and the substitution of aromatic carbons by polarizable heteroatoms.

The first approach is well illustrated by the tetrathiatetracene (TTT),<sup>1</sup> tetraselenatetracene (TSeT),<sup>2</sup> and tetratelluratetracene (TTeT)<sup>3</sup> sequence, where planar dichalcogenide bridges involving chalcogens of increasing size are branched on tetracene (T). The substituted molecules have a much better electron-donating character,<sup>4,5</sup> as can be observed from their solid-phase ionization potentials<sup>4</sup> (T 1.5, TTT 0.9, and TSeT 1.1 eV) and the good conducting properties of their charge-transfer complexes. For example, TTT<sub>2</sub>I<sub>3</sub> exhibits a room-temperature conductivity of  $10^3 \Omega^{-1} \text{cm}^{-1}$ .<sup>6</sup>

Examples of the second synthetic approach are bipyranlydene (BIPO)<sup>7</sup> and bithiopyranylidene (BIPS),<sup>8</sup> which can be viewed as resulting from the replacement of two CH groups in biphenyl (BIP) by oxygen or sulphur. The tetraphenyl substituted analogues<sup>7,8</sup> BIPOPh<sub>4</sub> and BIPSPH<sub>4</sub> (Figure 1). have been synthesized, and their respective radical-cation salts complexed with electron acceptors such as iodine or 7,7,8,8-tetracyanoquinodimethane (TCNQ)<sup>9-15</sup> The net result here is also a substantial reduction of the ionization potentials (BIP 3.0<sup>16</sup> and BIPSPH<sub>4</sub> 1.2 eV<sup>17</sup>). In the case of tetraphenyl-bithiopyranylidene polyiodides, conductivities as high as  $250\text{--}300 \Omega^{-1} \text{cm}^{-1}$ <sup>9-15</sup> have been reported.

It is interesting to note that TTT forms better conducting complexes than BIPSPH<sub>4</sub>.<sup>10</sup> In fact, contrary to planar TTT, a dihedral angle, defined by the planes of the two connecting heterocycles (Figure 1) exists in BIPSPH<sub>4</sub> and too strong a variation of this angle upon charge transfer can affect the conductivity, by increasing the intermolecular packing distances and therefore decreasing the  $\pi$  molecular overlap. It must be noted that the conductivity is better in TTT<sub>2</sub>I<sub>3</sub> than in the BIPSPH<sub>4</sub> salts, while the interface spacings are  $3.32 \text{ \AA}$ <sup>18</sup> and  $3.64\text{--}3.68 \text{ \AA}$ <sup>15,19</sup> respectively. In the experiments that report changes in structural (substitution at the system periphery, modification by replacing ring carbons by heteroatoms in the basic skeleton) and electrical properties of BIPSPH<sub>4</sub> when involved in charge-transfer complexation,<sup>8-15</sup>



X = O	R = H	BIPO
X = O	R = Ph	BIPOPh <sub>4</sub>
X = S	R = H	BIPS
X = S	R = Ph	BIPSPH <sub>4</sub>

Figure 1. Schematic molecular structures of the compounds

few attempts have been made to relate these variations to the electronic structure and thereby establish a theoretically based mechanism of the structural changes inducible in BIPSPH<sub>4</sub> by oxidation.

In this paper, we have performed *ab initio* calculations on three model molecules [biphenyl (BIP), bipyranlydene (BIPO), and bithiopyranylidene (BIPS)], and identified the main electronic-structure characteristics which are relevant to the interpretation of the structural features and electrical properties of BIPSPH<sub>4</sub> and related compounds.

### Computational Details

Because of computational limitations owing to the size of our model molecules, this study has been based on restricted Hartree-Fock-Roothaan results obtained with the strict minimal STO-3G basis set,<sup>20,21</sup> *i.e.*, without *3d* functions on the sulphur atoms. Nevertheless we have confidence in the reliability of our conclusions since previous works<sup>22,23</sup> have shown that introducing *3d* functions in the strict minimal basis merely reduces the polarity of C-S bonds without drastically changing the overall bonding picture. Calculations have been performed with the GAUSSIAN 80 program on a DEC 2060 computer; all integrals larger than  $10^{-6}$  have been taken into account and the convergence threshold on density matrix elements has been set to  $5 \times 10^{-5}$ .

Geometries of the model molecules were fixed with bond lengths and bond angles chosen with reference to previous experiments (BIP,<sup>24</sup> BIPO,<sup>25</sup> and BIPS<sup>26</sup>). Phenyl rings were replaced by hydrogen, for computational cost reasons. A main departure from the experimental solid-state structures

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**Table 1.** Electronic charges and Mulliken populations of biphenyl (BIP), bipyranylidene (BIPO), and bithiopyranylidene (BIPS)

Parameter		Biphenyl	BIPO	BIPS
Total energy (a.u.)		-454.628 82	-526.247 83	-1 164.830 06
Electronic charge	atom no. 1	C: 6.074	O: 8.230	S: 15.768
	C(2)	6.061	5.946	6.190
	C(3)	6.067	6.098	6.097
	C(4)	5.999	6.011	6.008
$\pi$ -Overlap populations	atom no. 1-C(2)	0.112	0.023	0.018
	C(2)-C(3)	0.105	0.175	0.176
	C(3)-C(4)	0.110	0.033	0.036
	C(4)-C(4')	0.019	0.144	0.139

**Table 2.** Monoelectronic energy levels of biphenyl (BIP)

This work  $E_{\text{tot.}} = -454.628 82$  a.u. (planar) and  $-454.630 34$  a.u. (skew)

Level $D_{2h}$ ( $D_2$ ) C 1s	Energy (eV) (number of levels)		Assignment
	Planar	Skew	
	300.07 (2)	300.07 (2)	C(4) and sym
	300.05 (4)	300.06 (4)	C(3) and sym
	300.04 (4)	300.04 (4)	C(2) and sym
$1a_{1g}$ ( $1a$ )	30.36	30.35	C 2s
$1b_{3u}$ ( $1b_3$ )	29.59	29.59	C 2s
$2a_{1g}$ ( $2a$ )	27.23	27.23	C 2s
$1b_{2u}$ ( $1b_2$ )	26.18	26.15	C 2s
$1b_{1g}$ ( $1b_1$ )	25.83	25.85	C 2s
$2b_{3u}$ ( $2b_3$ )	25.46	25.46	C 2s
$2b_{2u}$ ( $2b_2$ )	21.71	21.65	C 2s
$3a_{1g}$ ( $3a$ )	21.64	21.63	C 2s
$2b_{1g}$ ( $2b_1$ )	20.57	20.63	C 2s, C 2p
$3b_{3u}$ ( $3b_3$ )	20.20	20.21	C 2s
$4a_{1g}$ ( $4a$ )	18.61	18.55	C 2p, C 2s
$4b_{3u}$ ( $4b_3$ )	17.32	17.36	C 2p, H 1s
$5a_{1g}$ ( $5a$ )	16.69	16.62	C 2s, H 1s
$3b_{2u}$ ( $3b_2$ )	15.96	15.92	C 2p
$5b_{3u}$ ( $5b_3$ )	15.64	15.69	C 2p, H 1s
$3b_{1g}$ ( $3b_1$ )	14.78	14.85	C 2p
$6a_{1g}$ ( $6a$ )	14.73	14.71	C 2p, H 1s
$4b_{2u}$ ( $4b_2$ )	14.71	14.63	C 2p, H 1s
$4b_{1g}$ ( $4b_1$ )	13.89	14.05	C 2p
$1b_{1u}$ ( $5b_1$ )	13.26	13.10	$\pi$
$5b_{2u}$ ( $5b_2$ )	12.49	12.44	C 2p
$6b_{3u}$ ( $6b_3$ )	12.33	12.39	C 2p, H 1s
$1b_{2g}$ ( $6b_2$ )	12.15	12.16	$\pi$
$5b_{1g}$ ( $6b_1$ )	11.71	11.79	C 2p, H 1s
$7a_{1g}$ ( $7a$ )	11.07	11.03	C 2p, H 1s
$2b_{1u}$ ( $7b_1$ )	9.04	8.93	$\pi$
$1b_{3g}$ ( $7b_3$ )	7.49	7.47	$\pi$
$1a_{1u}$ ( $8a$ )	7.40	7.42	$\pi$
$2b_{2g}$ ( $7b_2$ )	6.80	6.88	$\pi$
(HOMO)			
$3b_{1u}$ ( $8b_1$ )	+ 6.20	+ 6.31	$\pi$
(LUMO)			

**Table 3.** Monoelectronic energy levels of bipyranylidene (BIPO)

Level	Energy (eV) (number of levels)	Assignment
O 1s	-553.22 (2)	O
C 1s	301.75 (2)	C(2)
	301.74 (2)	C(2)
	300.01 (2)	C(4)
	299.94 (4)	C(3)
$1a_{1g}$	36.67	O 2s
$1b_{3u}$	36.66	O 2s
$2a_{1g}$	29.36	C 2s, O 2s
$2b_{3u}$	27.64	C 2s, O 2s
$1b_{2u}$	27.29	C 2s
$1b_{1g}$	27.09	C 2s
$3a_{1g}$	24.24	C 2s, O 2s
$2b_{2g}$	22.23	C 2s, O 2p
$3b_{3u}$	21.46	C 2s, O 2p, O 2s
$2b_{1g}$	21.24	C 2s, C 2p, O 2p
$4a_{1g}$	19.13	C 2p, O 2p
$5a_{1g}$	17.80	C 2s, O 2s, H 1s
$4b_{3u}$	17.34	C 2p, O 2s, O 2p
$3b_{2u}$	17.04	C 2p, O 2p
$5b_{3u}$	16.35	C 2s, C 2p, H 1s
$3b_{1g}$	16.04	O 2p, C 2p
$4b_{2u}$	15.86	C 2p, O 2p, H 1s
$4b_{1g}$	15.10	C 2p, H 1s
$1b_{1u}$	14.78	$\pi$
$1b_{2g}$	14.54	$\pi$
$6a_{1g}$	13.89	C 2p, O 2p
$5b_{2u}$	13.12	C 2p, O 2p, H 1s
$2b_{1u}$	11.40	$\pi$
$5b_{1g}$	11.35	C 2p, O 2p
$6b_{3u}$	11.30	O 2p
$7a_{1g}$	11.14	O 2p, C 2p, O 2s
$1b_{3g}$	9.18	$\pi$
$1a_{1u}$	9.08	$\pi$
$2b_{2g}$	8.48	$\pi$
$3b_{1u}$ (HOMO)	3.76	$\pi$
$3b_{2g}$ (LUMO)	+ 5.37	$\pi$

has been conceded by assuming total planarity and  $D_{2h}$  symmetry, except for biphenyl, where another calculation, with a dihedral angle of  $23^\circ$ , has also been performed. Besides a reduction in the computational labour, justification for this choice was to provide a consistent comparison of the electronic structure of all compounds put on similar grounds. Accordingly, overlap and gross atomic populations and one-electron states are to be viewed here as transient references by which to assess substitutional effects and their consequences as to what structural features should eventually prevail.

## Results and Discussion

Table 1 lists total energies, gross atomic and  $\pi$ -overlap populations of BIP, BIPO, and BIPS. Total energies have a purely indicative purpose since no geometry optimization was carried out, and the  $\sigma$ -overlap populations have been omitted, owing to non-significant variations exhibited in this series of compounds. In what follows, we first proceed through an analysis of electronic structure of the neutral molecules and identify the dependence of the results on the particular

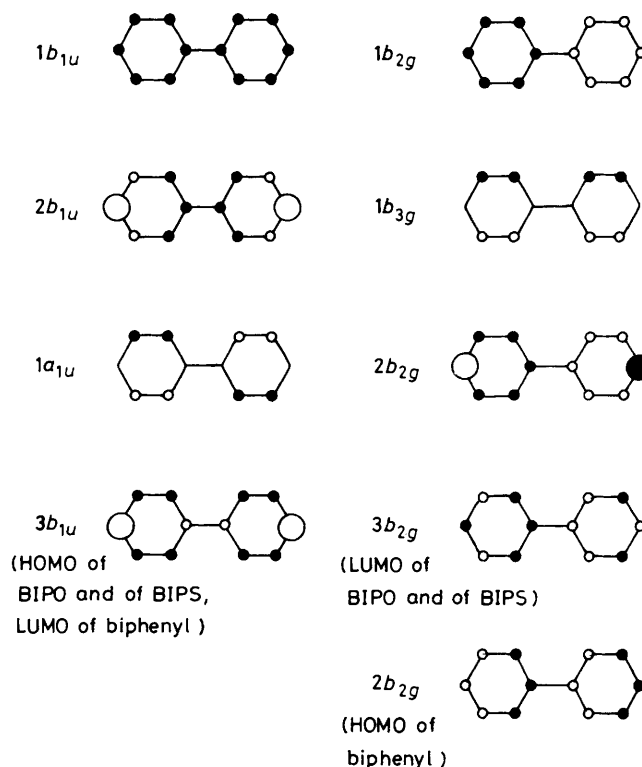
**Table 4.** Mono-electronic energy levels of bithiopyranylidene (BIPS)

Level	Energy (eV) (number of levels)	Assignment
S 1s	-2 470.71 (2)	S
C 1s	300.17 (4)	C(2)
	300.06 (2)	C(4)
	299.91 (4)	C(3)
S 2s	236.57 (2)	S
S 2p	172.16 (2)	S
	172.08 (2)	S
	172.03 (2)	S
1a <sub>1g</sub>	30.17	C 2s, S 3s
1b <sub>3u</sub>	29.37	C 2s, S 3s
1b <sub>2u</sub>	27.27	C 2s
2a <sub>1g</sub>	27.16	C 2s, S 3s
1b <sub>1g</sub>	29.96	C 2s
2b <sub>3u</sub>	25.03	S 3s, C 2s
3a <sub>1g</sub>	22.93	S 3s, C 2s
2b <sub>2u</sub>	22.00	C 2s
3b <sub>3u</sub>	21.27	C 2s, C 2p, S 3s
2b <sub>1g</sub>	20.69	C 2s, C 2p
4a <sub>1g</sub>	18.79	C 2p, C 2s
5a <sub>1g</sub>	17.88	S 3s, C 2s, C 2p, H 1s
4b <sub>3u</sub>	16.74	S 3s, C 2s, C 2p, H 1s
3b <sub>2u</sub>	16.14	C 2p
5b <sub>3u</sub>	16.05	C 2p, S 3p, C 2s
4b <sub>2u</sub>	15.58	S 3p, C 2p
3b <sub>1g</sub>	15.49	C 2p, H 1s
4b <sub>1g</sub>	14.08	C 2p, S 3p
1b <sub>1u</sub>	13.10	π
6a <sub>1g</sub>	13.02	C 2p, S 3p
5b <sub>2u</sub>	12.21	S 3p, C 2p
1b <sub>2g</sub>	11.89	π
5b <sub>1g</sub>	11.02	S 3p, C 2p
7a <sub>1g</sub>	10.08	S 3p
6b <sub>3u</sub>	9.91	S 3p
2b <sub>1u</sub>	9.46	π
1b <sub>3g</sub>	9.11	π
1a <sub>1u</sub>	8.98	π
2b <sub>2g</sub>	7.17	π
3b <sub>1u</sub> (HOMO)	3.55	π
3b <sub>2g</sub> (LUMO)	+4.90	π

geometries chosen in this work. Then, on the basis of this analysis, and using biphenyl as a reference point, we consider the possible structural changes induced in BIPO and BIPS upon oxidation.

Gross atomic charges on the ring atoms follow different trends if substitution is made with oxygen or sulphur. In the case of BIPO, oxygen bears a substantial negative charge essentially at the expense of C(2); C(3), and C(4) are slightly negative. By contrast, sulphur is predicted to be positive in BIPS and its electron deficit is balanced by negative populations on C(2), C(3), and C(4). In both cases, gross atomic charge on C(3) and C(4) remains insensitive to substitution.

The replacement of an aromatic carbon by chalcogens is strongly reflected in the evolution of π-overlap populations from biphenyl to BIPO and BIPS. In biphenyl, all π-overlap populations of endocyclic bonds are almost identical and the aromaticity picture of the benzene ring is unaffected by the C(4)-C(4') link. Substitution by chalcogen atoms in the 1 and 1' positions destroys this status: all bonds parallel to the principal axis of the molecule [*e.g.*, C(2)-C(3) and C(4)-C(4')] assume an important double-bond character, while the X-C(2) and C(3)-C(4) overlap populations are significantly reduced. Except for X-C(2), the π-overlap populations in both BIPO

**Figure 2.** π Molecular orbitals pictures of biphenyl (BIP), bi-pyranylidene (BIPO), and bithiopyranylidene (BIPS)

and BIPS are of comparable value and suggest that the nature of the chalcogen weakly affects the regulation of strong- and weak-bond alternation. The relatively small π-overlap populations on C(3)-C(4) and X-C(2) tend to indicate the existence of internal strains forcing the heterocycles to depart from a purely planar situation. Without geometry optimization, very little can be said on the directions along which the systems are ready to relax. Nevertheless, X-ray diffraction data on BIPOPh<sub>4</sub><sup>25</sup> and BIPSPPh<sub>4</sub><sup>26</sup> show the heterocycles favouring boat-like conformations.

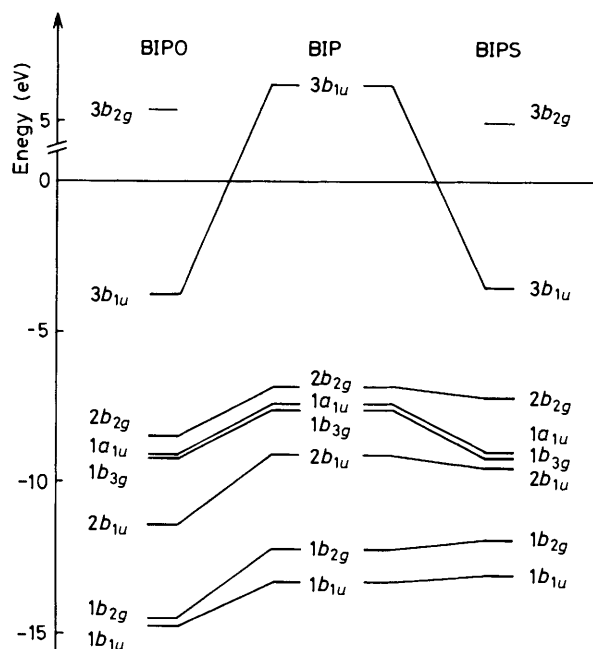
The one-electron state energies and symmetries of BIP, BIPO, and BIPS are collected in Tables 2, 3, and 4, respectively; the nodal structure of the relevant π orbitals is schematically represented in Figure 2 and a corresponding correlation diagram given in Figure 3.

The sequence of the π states is similar for the three compounds (Figure 3), while the energies are noticeably different. For instance, the 1a<sub>1u</sub> and the 1b<sub>3g</sub> levels of each compound reveal important LCAO coefficients of the same parity on C(2) and C(3) but, due to shorter C(2)-C(3) interdistances used in BIPO (1.337 Å) and BIPS (1.339 Å) compared with BIP (1.416 Å), a stronger stabilization is expected for the levels in BIPO and BIPS. In the same way, the remaining π levels are more stabilized in BIPO than in BIPS because of the large difference of the X-C(2) bond length (BIPO 1.389 and BIPS 1.745 Å) combined with a significant dissimilarity in their electronegativity.

The substitution by oxygen or sulphur adds two π electrons and the symmetry of the HOMO in both BIPO and BIPS is the same (3b<sub>1u</sub>) as for the LUMO of BIP. In agreement with<sup>16,17</sup> solid-state X-ray photoelectron spectroscopy data on BIP (3.0 eV) and BIPSPPh<sub>4</sub> (1.2 eV), the HOMO is located at higher values on the energy scale for BIPO (3.76 eV) and BIPS (3.55 eV) than BIP (6.8 eV). This shows the favourable influence of

**Table 5.** Evolution of the bond lengths (Å) in the bithiopyranylidene series

Bond	BIOPh <sub>4</sub> (ref. 25)	BIPSPh <sub>4</sub> (ref. 26)	BIPSPh <sub>4</sub> ·2.28I (ref. 19)	BIPSPh <sub>4</sub> ·3.3I (ref. 19)	BIPS <sub>2</sub> ·TCNQ (ref. 13)	TMBIPS·TCNQ (ref. 11)
X(1)–C(2)	1.389	1.745	1.715	1.729	1.702	1.710
C(2)–C(3)	1.337	1.339	1.366	1.360	1.351	1.360
C(3)–C(4)	1.443	1.441	1.442	1.417	1.418	1.431
C(4)–C(4')	1.385	1.389	1.442	1.447	1.429	1.435
Dihedral angle (°)	0	0	20.9	20.7		

**Figure 3.** Correlation scheme of the  $\pi$ -electronic levels of biphenyl (BIP), bipyranylidene (BIPO), and bithiopyranylidene (BIPS)

the substitution of C–H in biphenyl by oxygen or sulphur to reduce the ionization potentials. However, the change is weak in going from O to S and the same is expected to occur on the seleno- and telluro-derivatives, BIPSe and BIPTe.

We can now use this information on the electronic structure of the neutral model molecules to investigate possible geometry readjustments likely to take place in BIPO and BIPS when submitted to oxidative complexation. The following discussion refers implicitly to the concept of frontier orbitals. As frequently reported<sup>27</sup> and also verified above, the HOMO  $\pi$ -overlap populations mimic rather closely the structural features of the stable geometry. A stronger oxidation by electron acceptors will roughly correspond to a progressive depopulation of the HOMO and a concomitant decrease of both antibonding and bonding pairs present in this orbital (Figure 2). This usually leads to a geometry relaxation.

There are two major points to study as a function of complexation with electron acceptors: the resulting aromaticity pattern of the heterocycles, and its influence on the molecular geometry between them. Indeed, relaxation energy favouring (or not) the cation stabilization and the departure toward (or from) planarity are both related to the efficiency of charge carrier generation and transportation (the latter being eventually connected to propitious stacking modes).

On inspecting the nodal structure of BIPO and BIPS (Figure 2), it appears that a depopulation of the HOMO should result in a reduction of the bonding strength between

the heterocycles and on C(2)–C(3) as well as of the antibonding character of X–C(2) and C(3)–C(4). The net result is therefore a tendency towards bond equalization on the heterocycles (increased aromaticity on return to a more planar situation) accompanied by an increase in the dihedral angle between the two cycles. Calculated results are in general agreement with experimental results, due to the reduction of the *trans*-ring delocalization energy, *e.g.*, equalization of endocyclic bond length is confirmed by experimental results on charge-transfer complexes of BIOPh<sub>4</sub> with iodine and TCNQ (Table 5). Each (thio)pyranylidene moiety becomes planar, while this is not the case for neutral BIPSPh<sub>4</sub> and BIOPh<sub>4</sub>. Finally, *X*-ray diffraction data report a dihedral angle of *ca.* 0° between the two moieties in neutral BIOPh<sub>4</sub><sup>25</sup> and BIPS<sub>4</sub><sup>26</sup> while similar measurements on BIPSPh<sub>4</sub>·2.28I and BIPSPh<sub>4</sub>·3.3I find this angle to be *ca.* 21°.<sup>19</sup>

Although it was not the purpose of this paper, it is nevertheless interesting to note that biphenyl responds in an opposite way to electron withdrawal, as can also be understood from the nodal structure given in Figure 2.

Very little can be added to the structural changes in relation to the electronic structure of our model compounds. However, a more quantitative knowledge of actual geometries and a measure of the ability of those systems to stabilize the cationic forms could be obtained through extensive geometry optimization calculations. In such cases, other factors such as the steric hindrance between the *ortho*-hydrogen atoms on the two neighbouring rings would be taken into account. However, it should be kept in mind that, despite the heavy computational labour, the results would still correspond to isolated molecules, while crystal packing effects and especially long-range Coulomb interactions might determine the final molecular structures and properties in the solid state, and should probably deserve as much attention.

## Conclusions

As a first step, the electronic structure of three model molecules (without substituents) taken in a planar conformation (biphenyl, bipyranylidene, and bithiopyranylidene) has been detailed. This theoretical basis allows us to understand the true geometry and to appreciate the essential factors regulating the structural changes (loss of the planarity, bond length variations) observed on related neutral compounds or on their radical-cations salts complexed with electron acceptors. The good agreement with experimental results allows a cautious generalization of the conclusions to the larger class of BIPX (X = O, S, Se, or Te) compounds. The first ionization potentials of these compounds are expected to be only slightly modified, especially on going from the sulphur to the selenium derivatives.

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