

## HeI Photoelectron Spectra of *o,o'*-Bridged Biphenyls by 2-X-Propylene (X = O, S, SO, NCH<sub>3</sub>) Chains

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HeI photoelectron (PE) spectra of 1,11-dimethyl-5,7-dihydro-dibenzo[c,e]oxepine (**1**), 1,11-dimethyl-5,7-dihydro-dibenzo[c,e]thiopyrrolone (**2**), 1,11-dimethyl-5,7-dihydro-dibenzo[c,e]thiopyrrolone-S-oxide (**3**), 1,6,11-trimethyl-6,7-dihydro-5H-dibenzo[c,e]azepine (**4**), and 5,11-dimethyl-4,5,6,10,11,12-hexahydro-5,11-diaza-dibenzo[ef,kl]heptalene (**5**) have been measured. The low energy region of the spectra has been analyzed using semiempirical PM3, AM1 and MNDO SCF MO calculations (assuming the validity of Koopmans' theorem (*Physica* **1** (1934) 104) as well as empirical arguments (Franck-Condon (FC) envelopes) and correlation with PE spectra of similar molecules. Their electronic structure might be responsible for their chemical properties.

### INTRODUCTION

Title compounds represent an interesting class of biologically active molecules. A series of substituted derivatives of 6,7-dihydro-5H-dibenz[c,e]azepine was found to be active hypolipidemic agents in rodents.<sup>1</sup> Treatment with 6,7-dihydro-5H-dibenz[c,e]azepine resulted in a reduction of cholesterol, neutral lipid and triglyceride in mouse and rat liver.<sup>2</sup>

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The dibenzothiepine systems were found to be very useful antidepressant and antihistamine agents, as well as potent neuroleptic agents and tranquillizers, which proved their practical usefulness in the treatment of schizophrenic psychoses.<sup>3</sup>

Here, we report PE spectra of compounds that are of practical importance in pharmacology and medicinal chemistry. The compounds can be viewed as *o,o'*-disubstituted and/or bridged biphenyls with one or two 2-X-propylene (X = O, S, SO, NMe) chains acting as bridges. Such bridges force the molecule into stable conformation of  $C_2$  (**1–4**) or  $D_2$  (**5**) symmetry, whose dihedral angle is determined by the molecular structure and intramolecular interactions. Their electronic structure is of interest since it might be crucial for elucidation of the way in which these molecules interact with the corresponding receptors in living organism.

PE spectra yield information on the ordering of electron energy levels in a molecule, levels which quantum chemistry connects to the high occupied orbitals in a molecule (Koopmans' theorem).<sup>4</sup> Quantum chemical calculations have also led to the conclusion that many chemical reactions are orbitally controlled, that is, such reactions depend mainly on the characteristics of the outer molecular orbitals. This makes the measurement of the highest occupied orbital energies substantial for the estimation of relative chemical reactivity. The frontier orbital (FO) approximation, though introduced some forty years ago by Fukui,<sup>5</sup> has found wide use in explaining the relative reactivity, chemoselectivity, and regioselectivity of molecules. However, it should be applied only to systems in which the FO is sufficiently well separated from the other MOs. Otherwise, orbitals close in energy should also be taken into consideration.<sup>6,7</sup>

TABLE I

Vertical ionization energies ( $E_{i,v}/\text{eV}$ ), orbital energies for five highest occupied levels (numbers in parentheses denote the number of the corresponding orbital), and dihedral angle ( $\vartheta/^\circ$ ) for **1**

$E_i/\text{eV}$	$-\varepsilon_i/\text{eV}$		
	PM3	AM1	MNDO
8.35	9.2 $\pi_s$	9.06 $\pi_s$	9.09 (43) $\pi_s$
8.85	9.48 $\pi_a - n_O$	9.4 $\pi_a - n_O$	9.4 (42) $\pi_a - n_O$
	9.62 $\pi_a + n_O$	9.53 $\pi_a + n_O$	9.45 (41) $\pi_a + n_O$
9.20	9.98 $\pi_s + n_O$	9.93 $\pi_s + n_O$	9.78 (40) $\pi_s + n_O$
9.55	10.63 $n_O$	10.55 $n_O$	10.79 (39) $n_O$
$\vartheta/^\circ$	53.99	52.72	59.07

PE spectra of biphenyl and its derivatives have been reported before as well as quantum chemical calculations on them. Besides the ordering of the four high energy  $\pi$ -levels resulting from the interaction of two coupled phenyls, their energy dependence on conformation and steric effects was thoroughly investigated.<sup>8,9</sup>

## EXPERIMENTAL

The HeI PE spectra were measured on a Vacuum Generators UV-G3 photoelectron spectrometer<sup>10</sup> under 25 meV (FWHM) resolution.

Preparation of all compounds **1**,<sup>11</sup> **2**,<sup>12</sup> **3**,<sup>13</sup> **4**<sup>14</sup> and **5**<sup>11</sup> has been described.

Sample inlet temperatures were 100, 110, 170, 100 and 140 °C for **1–5**, respectively, in order to generate sufficient vapour pressure in the ionization region. The energy scale was calibrated by addition of a small amount of Xe to the sample gas flow.

The standard MOPAC 7.0 program package and PM3, AM1 and MNDO Hamiltonians were used in the calculations, with full geometry optimization being performed during calculations. Input geometries were optimized initially using the molecular mechanics [MM2] method.

## RESULTS AND DISCUSSION

The HeI PE spectra with the corresponding correlation diagrams of **1–2**, **2–3** and **4–5** are shown in Figures 1 and 2–4, respectively. Vertical ionization energies,  $E_{i,v}$  or energies of broad band maxima, are indicated atop the corresponding band systems.

As a result of the present study, molecular orbital pictures based on PM3 calculations are assigned to the corresponding experimental ionization energy values in the correlation diagrams (Figures 2–4).

The dominant feature of all the spectra are the overlapping bands in the low energy region, whereas calculations predict a high density of ionic states in the higher energy region ( $E_i > 11$  eV), thus making Koopmans' analysis of not much use.

Since all the compounds are bridged nonplanar biphenyls, the ionization events associable with perturbed  $\pi$ -benzene orbitals and  $n_x$  lone pair orbitals of the heteroatom(s) in the bridge(s) are expected to occur in this region. With almost no symmetry restrictions on orbital mixing, the interaction takes place predominantly between orbitals that are close in energy.

**1,11-Dimethyl-5,7-dihydro-dibenzo[c,e]oxepine (1)**. The crucial constituent part of the title compounds is a biphenyl moiety with two *o,o'*-Me-groups in »cisoid« position. Intramolecular steric repulsion in such *o,o'*-

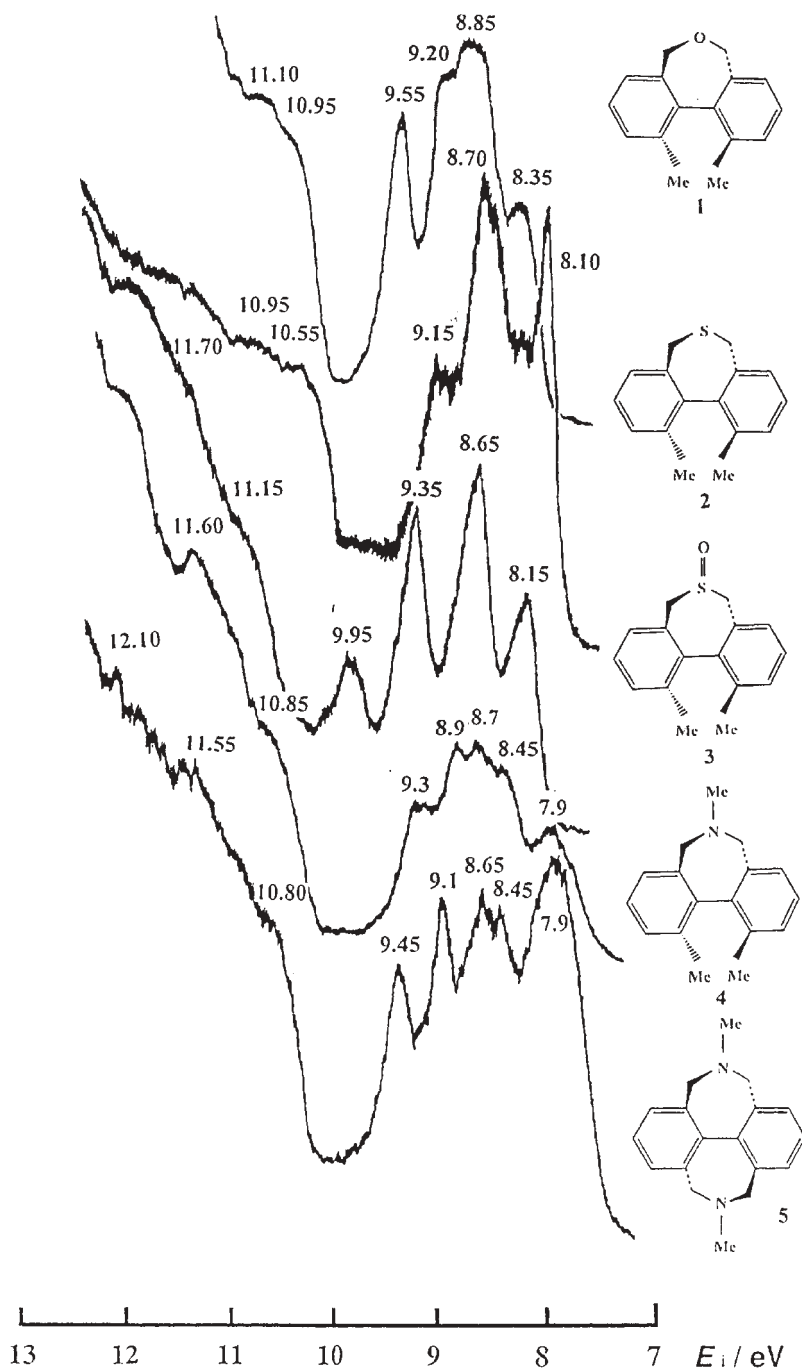


Figure 1. HeI PE spectra of compounds 1-5.

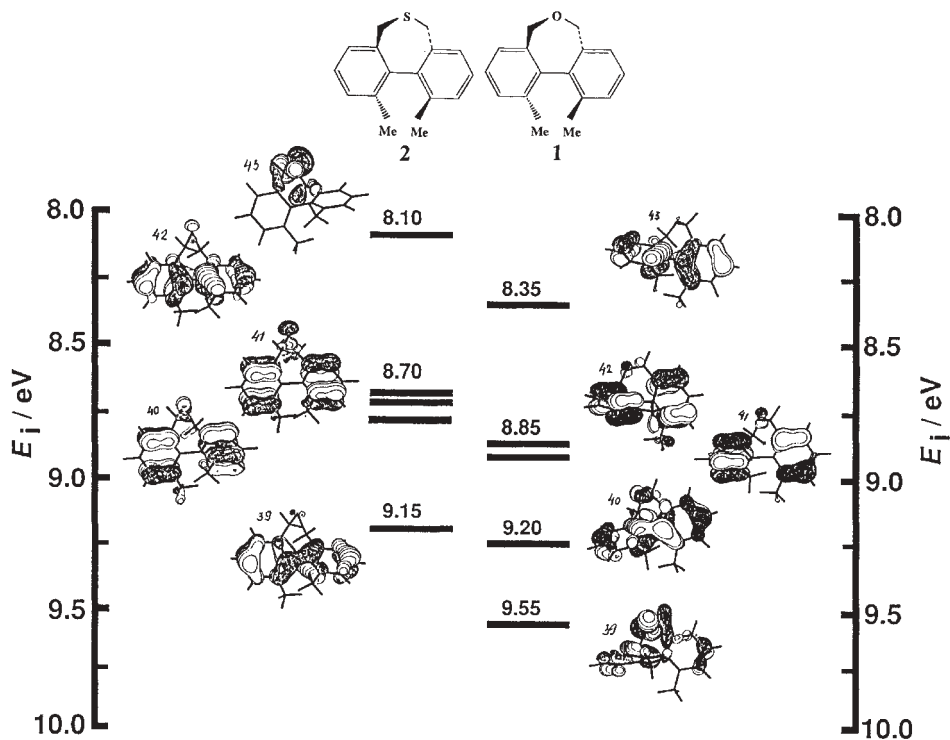


Figure 2. The proposed assignment of the low energy region of the HeI PE spectra of compounds 1–2 based on the quantum chemical results of PM3.

disubstituted biphenyl prevents the rings to be coplanar, and would be lowest for them being mutually perpendicular. Benzene  $\pi$ - $\pi$  interaction, on the other hand, tends to keep the phenyl groups coplanar. To deduce the effective dihedral angle, both effects should be taken into account. On the basis of ORD, CD, GL chromatography retention times, the inferred dihedral angle of 2,2'-diMe-biphenyl<sup>8,9</sup> is 78° whereas the gas-phase electron diffraction data, and multiconfigurational second-order perturbation theory results (CASPT2)<sup>15</sup> on biphenyl yield values of 44.4° and 44.3°, respectively. This change in dihedral angle is evident in their PE spectra.<sup>8,9</sup> With increased dihedral angle, the splitting of the linear combinations of symmetric,  $\pi_s$ , benzene orbitals becomes smaller, whereas the two asymmetric,  $\pi_a$ , combinations are almost unaffected (the orbitals are accidentally degenerate). As a result, the four outmost ionization energies in biphenyl are at 8.32, 9.25 (doubly degenerate) and 9.80 eV, and at 8.55, 8.90 (doubly degenerate), and 9.25 eV in 2,2'-diMe-biphenyl. The overlapping of the bands in the latter is much more pronounced.

Except for interactions of two benzene moieties, the through-space (TS) interaction with the oxygen (or other heteroatom) lone-pair and/or through-bond (TB) [*via*  $\sigma$  alkane skeleton] orbital mixing may take place in the bridged molecules. [One has to bear in mind that TS/TB effects are separable only within the limits of a theoretical model].<sup>16</sup> With this in mind, the interpretation of the low energy region of the PE spectrum of **1** is quite straightforward. All the semiempirical quantum chemical calculations [PM3, AM1, MNDO] give the same orbital-type ordering [see correlation diagram, Figure 2]. The lowest energy ionization is assigned to the antisymmetric linear combination of two  $\pi_s$ , with no contribution from oxygen lone-pair orbital. Based on its relative intensity, the band maximum at 8.85 eV is assigned to two ionizations, namely from linear combinations of  $\pi_a$  with oxygen 2p orbitals. The system at 9.20 eV is assigned to ionization from symmetric combination of  $\pi_s$  with some oxygen lp participation. The system at 9.55 eV corresponds to ionization from an orbital of primarily oxygen parentage, which is confirmed by both quantum chemical calculations and comparison with the spectra of other ether type molecules.<sup>17,18</sup>

**1,11-Dimethyl-5,7-dihydro-dibenzo[c,e]thiepine (2).** The PE spectra of open chain and cyclic alkyl sulphides all have their lowest ionization energy in the region of 8–9 eV, depending on the number of alkyl groups present. Their first electronic system corresponds to the ionization event from  $n_s/\sigma_{CH_2}$  orbital.<sup>19,20</sup>

However, in **2**, the linear combinations of four benzene  $\pi$ -orbitals give rise to four closely spaced electronic systems in that same energy region. Thus, TS/TB mixing with the sulphur 3p lone pair orbital is expected. Quantum chemical calculations do not give a straightforward interpretation for the lowest ionization event. According to MNDO and AM1 results, the system should be assigned to the predominant antisymmetric linear combination of  $\pi_s$  benzene orbitals with only a minor  $n_s$  lone pair contribution. In contrast, PM3 calculation predicts a  $n_s/\sigma_{CH_2}$  orbital as HOMO. The first ionization system at 8.10 eV displays a FC envelope characteristic of a sulphur lone pair ionization (see PE spectrum). Therefore, we favour the interpretation given by PM3, which agrees also with expectations based on the PE spectra of similar compounds.

According to the PM3 results, the second (MO 42), third (MO 41) and fourth (MO 40) highest occupied orbitals are almost degenerate [accidental degeneracy] and their parentage is of  $\pi$ -benzene and sulphur ( $\sigma_s$ ) character [see Fig 2, Table 2]. Such an interpretation is consistent with the experimental findings, since the three systems with energy maximum at 8.7 eV extensively overlap with the resulting very broad envelope. The system with ionization maximum at 9.15 eV is ascribed to the symmetric linear combina-

tion of  $\pi_s$  orbitals, in which the participation of the sulphur orbital has only minor significance.

**1,11-Dimethyl-5,7-dihydro-dibenzo[c,e]thiepine-S-oxide (3).** In the PE spectrum of dimethylsulfoxide,<sup>21</sup> the first system at 9.01 eV is associated with  $[n_S-(n_O)]$  orbital, the second at 10.17 eV with  $[\pi_{SO} - (\sigma_{CS}^-)]$ , and the third at 12.57 eV with the  $[n_O-(\sigma_{CS}^+)]$ . Comparison with PE spectroscopic results for many other sulfoxides<sup>22,23</sup> supports our assignment [Figure 1 and correlation diagram in Figure 3] of the first system in **3** at 8.15 eV as  $[n_s-(n_O)]$  in agreement with PM3, AM1 and MNDO quantum chemical calculations. The relative intensities of the bands at 8.65 and 9.35 eV support the assumption that two ionization processes are operative in each case. On the basis of quantum chemical results, they are ascribed to linear combinations of mainly  $\pi$ -benzene parentage [see correlation diagram, Figure 3]. The system at 9.95 eV should then be assigned to ionization from a predominantly  $n_O$  type orbital. Much of the experimental evidence confirms such assignment. Unlike in phenylsulfoxide<sup>22</sup> compounds,  $\pi_{SO}$  in **3** is expected at energies  $>11.5$  eV [PM3 calculation assigns MO 38 to it].

**1,6,11-Trimethyl-6,7-dihydro-5H-dibenz[oc,e]azepine (4).** The PE spectrum of **4** (Figure 1) reveals overlapping bands that are expected to arise from benzene  $\pi$ -orbitals [dihedral angle amounts to  $60^\circ$  according to calculations], and  $n_N$  lone pair orbitals. Here again, the quantum chemical calculations differ in predicting the character of the lowest ionization energy. From MNDO and AM1 that ionization event is from a  $\pi_s/n_N$  combination orbital, whereas according to PM3 results this electronic system corresponds to ionization from a mainly  $n_N/\sigma_{CH_2}$  orbital. The observed broadness of the FC envelope at 7.9 eV favours the PM3 result. Namely, in a number of cyclic and

TABLE II

Vertical ionization energies ( $E_{i,v}/\text{eV}$ ), orbital energies for five highest occupied levels (numbers in parentheses denote the number of the corresponding orbital), and dihedral angle ( $\vartheta/^\circ$ ) for **2**

$E_i/\text{eV}$	$-\epsilon_i/\text{eV}$		
	PM3	AM1	MNDO
8.10	8.87 $n_S/\sigma_{CH_2}$	8.45 $\pi_s$	9.19 (43) $\pi_s$
8.7	9.31 $\pi_s/n_S$	9.1 $\pi_s/n_S$	9.38 (42) $\pi_a/n_S$
	9.48 $\pi_a/n_S$	9.31 $\pi_a/n_S$	9.39 (41) $\pi_a/n_S$
	9.58 $\pi_a/n_S$	9.41 $\pi_a$	9.46 (40) $n_S/\pi_a$
9.15	10.01 $\pi_s/n_S$	9.92 $\pi_s$	11.42 (39) $\pi_s$
$\vartheta/^\circ$	66.93	65.26	68.65

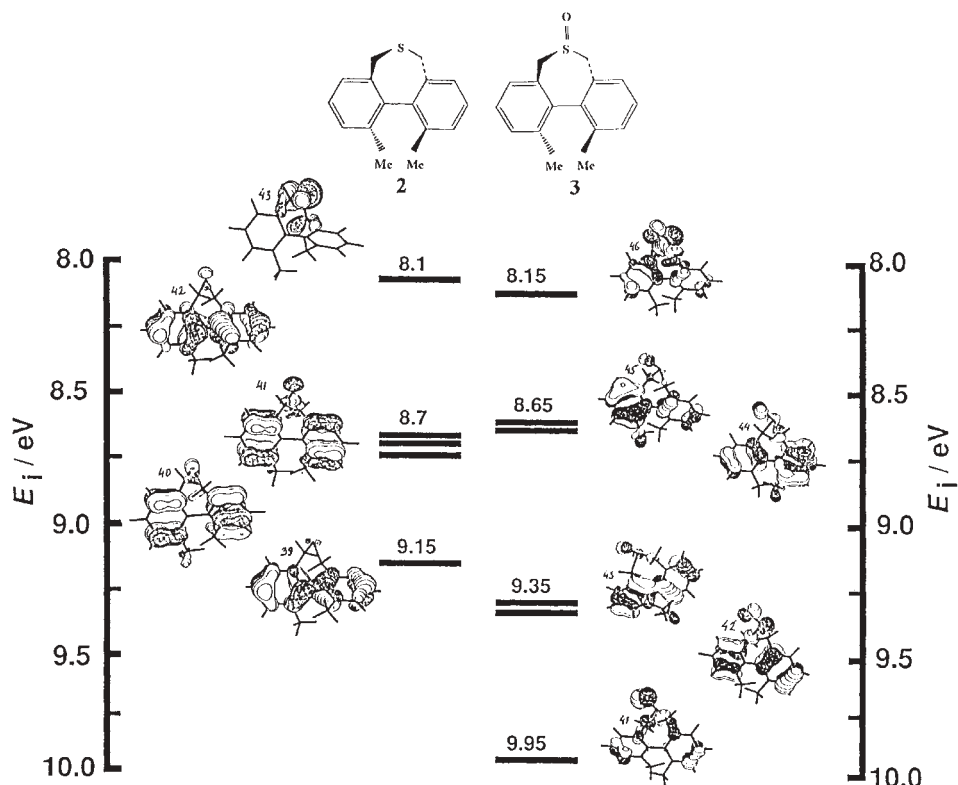


Figure 3. The proposed assignment of the low energy region of the HeI PE spectra of compounds **2–3** based on the quantum chemical results of PM3.

bicyclic amines<sup>24</sup> and morpholines,<sup>18</sup> the first ionization energy corresponds to  $n_N$  ionization accompanied by a substantial change in geometry. The vibrational structure is lost as a consequence of extensive mixing with  $\sigma_{CH_2}$  orbitals.

The following three strongly overlapping systems at 8.45, 8.70 and 8.90 eV as well as the next one at 9.3 eV are assigned to ionizations from linear combinations of  $\pi$ -benzene and  $n_N$  orbitals (see correlation diagram, Figure 4).

**5,11-Dimethyl-4,5,6,10,11,12-hexahydro-5,11-diazadibenzo[ef,kl]heptalene (5)**. Relative intensities of the PE spectra of **4** and **5** show that in **5** the first system has gained significantly in intensity, yet its position [ $E_{i,v}$ ] has not changed [7.90 eV in both **4** and **5**]. Interpretation of such behaviour is based on comparison with the PE spectra of bicyclic diamines<sup>24,25</sup> where the two  $n_N$  lone-pair linear combinations are nearly degenerate, *i.e.* the net



TABLE III

Vertical ionization energies ( $E_{i,v}/\text{eV}$ ), orbital energies for five highest occupied levels (numbers in parentheses denote the number of the corresponding orbital), and dihedral angle ( $\vartheta/^\circ$ ) for **3**

$E_i/\text{eV}$	$-\varepsilon_i/\text{eV}$		
	PM3	AM1	MNDO
8.15	8.97 [ $n_s-(n_O)$ ]	8.98 [ $n_s-(n_O)$ ]	9.19 (46) [ $n_s-(n_O)$ ]
8.65	9.44 $\pi_s/\pi_a$	9.23 $\pi_s/\pi_a$	9.40 (45) $\pi_s/\pi_a$
	9.52 $\pi_s/\pi_a$	9.37 $\pi_s/\pi_a$	9.51 (44) $\pi_s/\pi_a$
9.35	9.94 $\pi_s/\pi_a$	9.60 $\pi_s/\pi_a$	9.87 (43) $\pi_s/\pi_a$
	10.06 $\pi_s/\pi_a$	10.01 $\pi_s/\pi_a$	10.06 (42) $\pi_s/\pi_a$
9.95	10.68 $n_O$	11.19 $n_O$	10.37 (41) $n_O$
$\vartheta/^\circ$	62.5	61.0	67.35

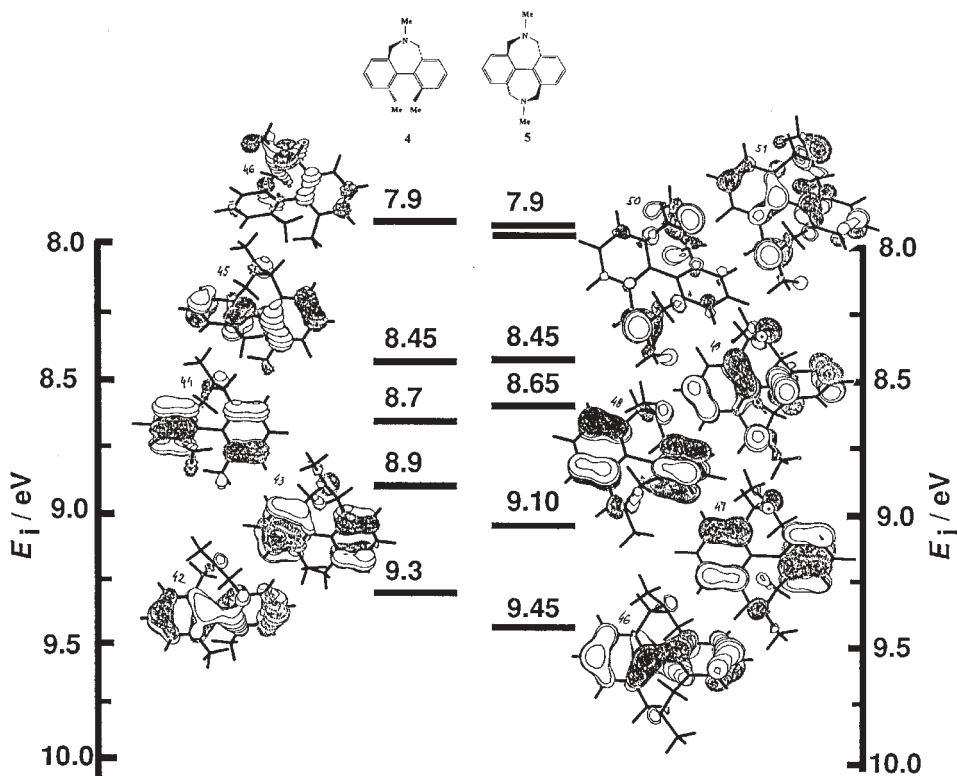


Figure 4. The proposed assignment of the low energy region of the HeI PE spectra of compounds **4-5** based on the quantum chemical results of PM3.

TABLE IV

Vertical ionization energies ( $E_{i,v}/\text{eV}$ ), orbital energies for five highest occupied levels (numbers in parentheses denote the number of the corresponding orbital), and dihedral angle ( $\vartheta/^\circ$ ) for **4**

$E_i/\text{eV}$	$-\varepsilon_i/\text{eV}$		
	PM3	AM1	MNDO
7.9	8.92 $n_N/\sigma_{\text{CH}_2}$	8.87 $\pi_s/n_N$	8.98 (46) $\pi_s$
8.45	9.17 $\pi_s$	9.08 $n_N/\pi_s$	9.23 (45) $\pi_a/n_N$
8.70	9.42 $\pi_a$	9.31 $\pi_a$	9.31 (44) $\pi_a/n_N$
8.90	9.52 $\pi_a$	9.56 $\pi_a$	9.6 (43) $\pi_s/n_N$
9.30	9.70 $\pi_s$	9.95 $\pi_s/n_N$	9.96 (42) $\pi_s$
$\vartheta/^\circ$	55.96	53	60.04

TABLE V

Vertical ionization energies ( $E_{i,v}/\text{eV}$ ), orbital energies for five highest occupied levels (numbers in parentheses denote the number of the corresponding orbital), and dihedral angle ( $\vartheta/^\circ$ ) for **5**

$E_i/\text{eV}$	$-\varepsilon_i/\text{eV}$		
	PM3	AM1	MNDO
7.9	8.92 $n_N/n_N$	8.83 $\pi_s/n_N$	8.92 (51) $\pi_s/n_N$
	9.00 $n_N/n_N$	9.05 $n_N/n_N$	9.31 (50) $\pi_a/n_N$
8.45	9.32 $\pi_s/n_N$	9.28 $\pi_a/n_N$	9.36 (49) $\pi_a/n_N$
8.65	9.58 $\pi_a/n_N$	9.53 $\pi_s/n_N$	9.55 (48) $n_N/n_N$
9.10	9.81 $\pi_a/n_N$	9.76 $\pi_a/n_N$	9.66 (47) $\pi_s/n_N$
9.45	10.22 $\pi_s/n_N$	10.20 $\pi_s$	9.96 (48) $\pi_s$
$\vartheta/^\circ$	46.1	45.0	46.3

effect of TB/TS interaction negligibly splits the two systems. However, the two nitrogen atoms are obviously too far apart for TS interaction to be significant, and TB coupling is crucially dependent on the conformation within the bridges. PM3 results are strongly in favour of such an interpretation – orbital energies are  $-8.92$  and  $-9.00$  eV, respectively, and the orbital coefficients at N-positions are dominant (see correlation diagram, Figure 4.). Accordingly, the system at  $8.45$  eV results from ionization of an electron from antibonding  $\pi_s/n_N$ , the  $8.65$  eV system from antibonding  $\pi_a/n_N$ , whereas the systems at  $9.10$  eV from bonding  $\pi_a/n_N$  and at  $9.45$  eV from bonding  $\pi_s/n_N$  orbital linear combinations.

## CONCLUSION

The electronic structure of **1–5** could be assigned successfully although semiempirical quantum chemical calculations used in this work (PM3, AM1 and MNDO) gave the same ordering only for **1** and **3**. In the case of **2**, **4** and **5**, the interpretation of the HOMO character differed significantly. On the basis of experimental results, *e.g.* FC envelopes in the PE spectra of a similar type of compounds, HOMO in **2** is almost exclusively of  $n_S$  lone pair character, whereas in **4** and **5** it is of significant  $n_N$  lone pair character. Such assignment is supported only by the PM3 results, which thus seem to give the best agreement with experiment and are considered as the most reliable.

Electronic structure might be important for elucidation how these bioactive molecules interact with the corresponding receptors in living organisms.

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## SAŽETAK

### HeI fotoelektronski spektri bifenila *o,o'* – premošćenih 2-X-propilenskim lancem (X = O, S, SO, NCH<sub>3</sub>)

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Snimljeni su HeI fotoelektronski (PE) spektri 1,11-dimetil-5,7-dihidro-dibenz[c,e]oksepina (**1**), 1,11-dimetil-5,7-dihidro-dibenz[c,e]tiepina (**2**), 1,11-dimetil-5,7-dihidro-dibenz[c,e]tiepin-S-oksida (**3**), 1,6,11-trimetil-6,7-dihidro-5H-dibenz[c,e]azepina (**4**) i 5,11-dimetil-4,5,6,10,11,12-heksahidro-5,11-diaza-dibenz[ef,kl]heptalena (**5**).

Elektronski sustavi u području niskih ionizacijskih energija protumačeni su na temelju semiempirijskih kvantnokemijskih računa PM3, AM1 i MNDO [pretpostavljajući da vrijedi Koopmansovo približenje (*Physica* **1** (1934) 104.)] kao i empirijskih argumenata (Franck-Condonovi (FC) obrisi) te korelacije s PE spektrima sličnih molekula.

Elektronska struktura proučavanih spojeva mogla bi biti odgovorna za njihova kemijska svojstva.