

Photoelectron Spectroscopy of Heterocycles. Fluorene Analogues*

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The He(I) photoelectron spectra of fluorene and its analogues, biphenyl, dibenzofuran, carbazole, dibenzothiophene, and phenanthrene were measured and analyzed. The assignment of the π -electron ionizations using orbital interaction and symmetry arguments for the constituent parts of the molecules indicates that the energy levels of the fluorene analogues can be reproduced within a few percent of error. A close linear correlation between the π -ionization energies and the eigenvalues of the corresponding HMO-orbitals is obtained as well.

Introduction

The concept of analogues has proved to be useful for the elucidation of the electronic structure of conjugated heterocyclic molecules. This concept defines compounds derived from a "parent" hydrocarbon by replacing one of its CH_n -groups by a heteroatom or a heteroatom-containing group as analogues. Since the molecular properties and their relation to the electronic structure for the parent molecule are usually well known, changes in molecular properties within the analogues caused by the heteroatom may yield valuable information about their electronic structure, which usually is not readily accessible.

This procedure in a way allows to treat the effect of the heteroatom by two types of parameters: one describes the heteroatom introduced and the other accounts for its interaction with the residue of the parent molecule.

The application of the concept of analogues to photoelectron (PE) spectroscopy has been considered so far for π -ionizations only. The PE study of several heteroatom-substituted aromatic compounds revealed that for some heteroatoms or groups an additional parameter, generally known as inductive, had to be introduced to describe the σ - π interactions. In a first approximation this parameter is independent of the residue of the parent molecule, i.e., the molecule itself and the

position of the heteroatom introduced. Thus, once determined experimentally, the parameters should be transferable to other molecules.

In this paper we want to demonstrate the concept of analogues and the transferability of parameters obtained previously on the PE-spectroscopy of indene analogues [1] to the fluorene analogues, i.e., to molecules which can be thought to be obtained from fluorene by replacing its CH_2 group by two hydrogens (biphenyl), by $-\text{O}-$ (dibenzofuran), by $-\text{NH}-$ (carbazole), by $-\text{S}-$ (dibenzothiophene) and by $-\text{CH}=\text{CH}-$ (phenanthrene).

Experimental

PE spectra of biphenyl, fluorene, dibenzofuran, carbazole, dibenzothiophene, and phenanthrene were recorded on a Vacuum Generator UV-G3 instrument [2] with He(I) excitation at elevated temperature (biphenyl 60 °C, fluorene 115 °C, dibenzofuran 110 °C, carbazole 180 °C, dibenzothiophene 120 °C, and phenanthrene 110 °C) in the inlet system. During the recording step no decomposition of the samples was observed. Low resolution (30–50 meV) for the complete PE spectra, and high resolution (~ 15 meV) and expanded scale for some individual band system was used. The energy scale of the PE spectra was calibrated by the simultaneous addition of small amounts of argon, xenon, and nitrogen to the sample gas flow.

All compounds investigated were of commercial origin and were purified by recrystallization or sublimation before use. Fluorene was purified by zone melting.

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Theory

For all fluorene analogues investigated a HMO calculation was performed. The following heteroatom parameters [3] (X , h_X , and k_{CX} , respectively) were applied: \ddot{O} : 2.00, 0.9; $\ddot{N}H$: 1.00, 0.9; \ddot{S} : 1.00, 0.50; CH_3 and CH_2 : h_{CX} : -0.50 (inductive). The assignment of the π -ionizations was supported by a calculation involving diagonalization of the interaction matrices between the constituent parts of the molecule. The principles of this method have been demonstrated in a recent paper [1]. Although similar to the LCMO- and LCBO-methods [4, 5] this method uses experimental ionization energies and follows a somewhat different approach. Briefly, the molecule investigated is divided into the parent molecule and the heteroatom. The π -ionization energies, or, with the validity of Koopmans theorem, the π -orbital energies of both parts of the composite molecule constitute the diagonal elements of the matrix, while the off-diagonal elements are set to zero if the respective π -orbitals do not interact or to 1 eV if they do. This value is approximately half the value of the Hückel resonance integral β . The method is rather insensitive to meaningful values of the non-zero off-diagonal elements of the matrix. The eigenvalues obtained from diagonalization of the matrix must be corrected for an inductive effect which is a function of the difference between the ionization energies of the constituent parts (i.e., the sum diagonal elements of the interaction matrix) and the experimental π -ionization energies of the composite molecule. The correction is applied with the same weight to every eigenvalue and has a characteristic value for every heteroatom. This value can be estimated as

$$I = (\text{Tr} - \sum_{i=1}^n E_i)/n, \quad (1)$$

where Tr is the trace of the matrix, E_i are the experimental π -ionization energies, and n the number of π -orbitals. This represents a useful experimental approach for the determination of the magnitude of the inductive effect.

The calculation procedure described could be interpreted as an inversion of the method proposed by Simpson [6, 7] for π -electron spectra. In that method the given observed set of term values arranged along the diagonal of a square matrix is transformed into a non-diagonal form called the structure representation.

Application of the simple method of π -orbital assignment is demonstrated with the PE spectra of the fluorene analogues.

Results and Discussion

The full He(I) PE spectra of the fluorene analogues investigated are shown in Figures 1, 2, 4–7. The vertical ionization energies are given in eV (± 0.015 eV) over the appropriate position in the PE spectra. The values for diffuse and/or overlapping systems are not indicated. The assignment of the π -orbitals are given at the abscissa.

Fluorene and Biphenyl

The PE spectra of fluorene (Fig. 1) and biphenyl (Fig. 2) are well known [8], and the systems \tilde{X} , \tilde{A} , \tilde{B} , and \tilde{C} have been already assigned to photoionizations from the first four π -orbitals in both compounds. To attempt further assignment of the π -ionizations within the model of interaction matrix, one must consider a hypothetical planar biphenyl molecule constructed of two benzene units, since fluorene, unlike biphenyl, is planar. The π -ionizations of benzene were assigned as 9.23 eV (doubly degenerate π_2 and π_3 orbital) and 12.35 eV for π_1 [9]. The interaction matrix should allow the two benzene units to interact in the simplest way. Leaving out the π_2 orbitals (due to the nodal plane passing through the interacting centers), and allowing an interaction between identical orbitals results in a 4×4 matrix which can be separated into two 2×2 matrices (describing the interaction of π_1 and π_3 orbitals, respectively). This procedure furnishes the following results: 8.23, 9.23, 9.23, 10.23, 11.35, and 13.35 eV. The π -system of fluorene is essentially the same as in a planar biphenyl. Taking into account -0.3 eV for the inductive effect of the methylene group [1], i.e., adding this value to each of the upper results of biphenyl, assigns the \tilde{D} system at 11.04 eV to photoionization from the π_2 orbital. The photoionization from the π_1 orbital should be expected around 13.2 eV together with the σ -onset starting at ~ 11.3 eV (Figs. 1 and 3).

The electron diffraction study of biphenyl indicates an elevated dihedral angle [10]. Rotation of the benzene units along the connecting bond can be taken into account by destabilizing the π_1 and π_3 orbital by 0.5 eV. This value is approximately the off-diagonal interaction element multiplied by

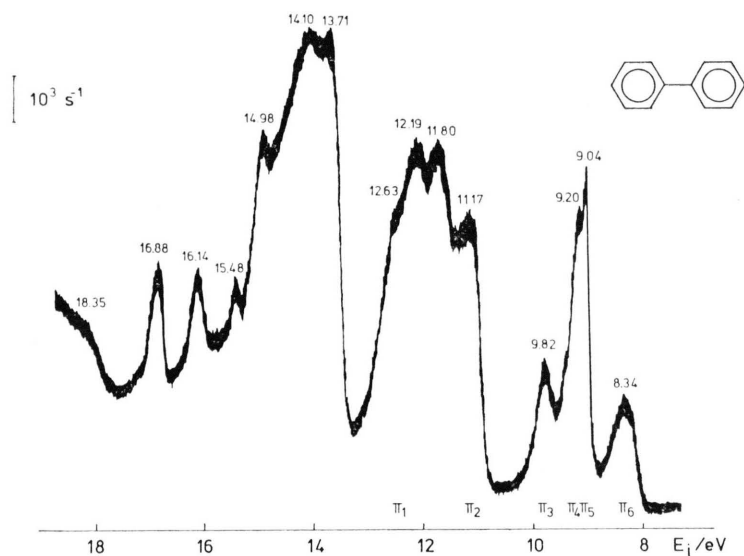


Fig. 2. He(I) photoelectron spectrum of biphenyl.

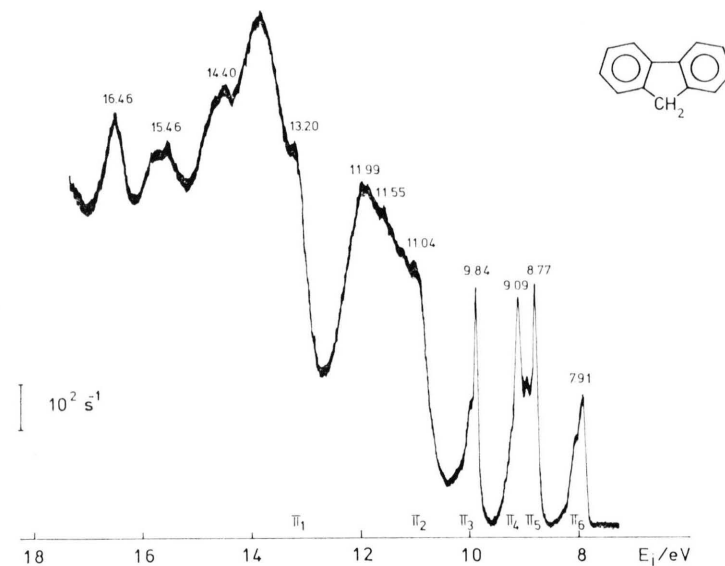


Fig. 1. He(I) photoelectron spectrum of fluorene.

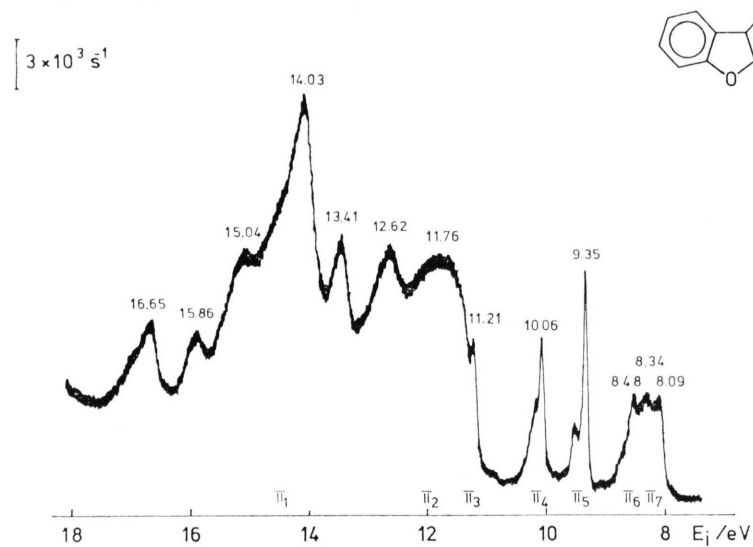


Fig. 5. He(I) photoelectron spectrum of dibenzofuran.

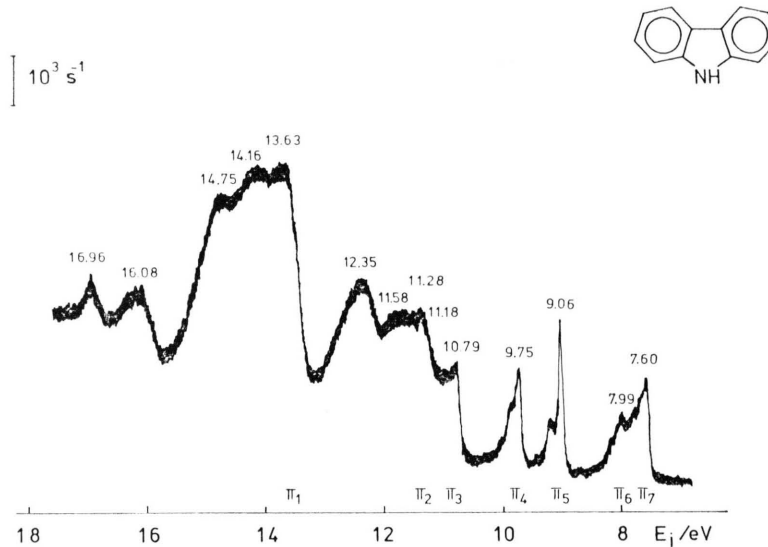


Fig. 4. He(I) photoelectron spectrum of carbazole.

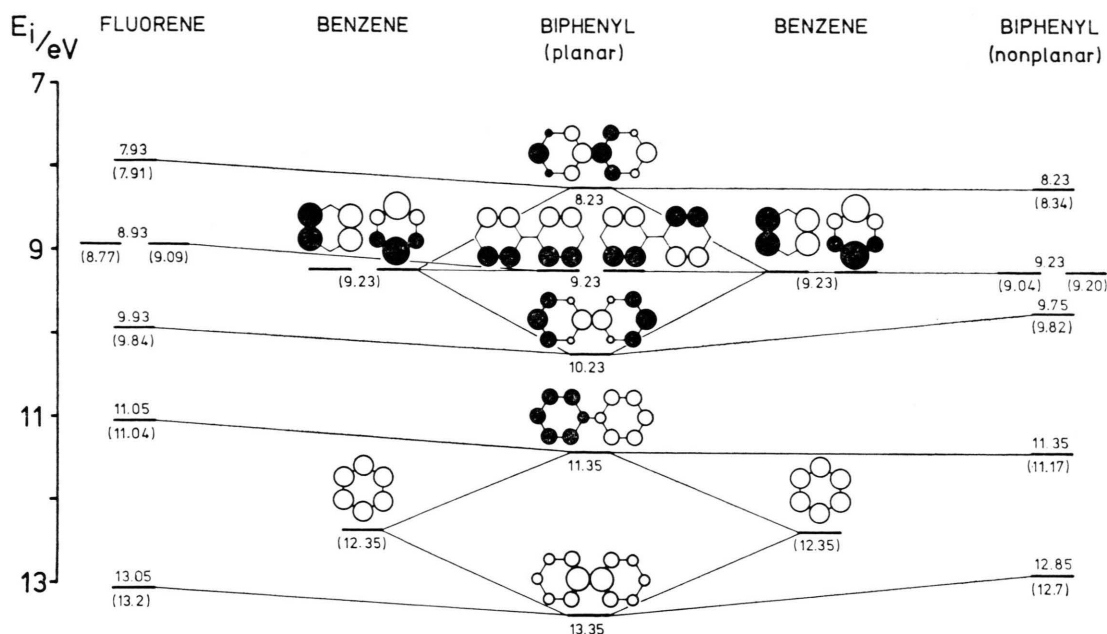


Fig. 3. Schematic representation of the matrix method of the π -ionization energies calculated in eV of biphenyl and fluorene. Experimental data are indicated in parentheses.

$\cos \varphi$. The rotation should not have an appreciable effect on the other orbitals because of the node in the middle of the bond. This allows to assign the \tilde{D} system of biphenyl at 11.17 eV to ionization from the π_2 orbital (Figs. 2 and 3). The ionization from the π_1 orbital should be expected around 12.6 eV. This assignment is supported by the linear correlation of the assigned π -ionizations with the HMO results (see Figure 8). The application of the method described nicely predicts the different location of the system arising from π_1 -ionization in the very similar PE spectra of fluorene and biphenyl.

Carbazole and Dibenzofuran

The PE spectra of carbazole (Fig. 4) and dibenzofuran (Fig. 5) have been reported [11, 12]. They exhibit a strong similarity to the PE spectra of biphenyl and fluorene. A recent CNDO study of carbazole shows that the \tilde{X} , \tilde{A} , \tilde{B} and \tilde{C} systems belong to π -ionizations [13]. The same assignment can be expected for the first four systems in dibenzofuran. However, the assignment of higher systems in both molecules is less certain. Again, assignment by the interaction matrix procedure is useful. It makes use of the results for planar biphenyl and either the nitrogen lone-pair energy in

ammonia of 10.85 eV for carbazole, or the oxygen lone-pair energy in water of 12.61 eV for dibenzofuran [14]. The π_2 , π_5 and π_6 orbitals of the planar biphenyl have a nodal plane separating the two benzene units. Obviously, a lone-pair of nitrogen or oxygen cannot be antisymmetric to this plane, thus, the appropriate interaction elements must be zero, i.e., these orbitals are not introduced into the matrix. In the case of carbazole this gives:

$$\begin{pmatrix} 9.23 & 0 & 0 & 1.0 \\ 0 & 10.23 & 0 & 1.0 \\ 0 & 0 & 13.35 & 1.0 \\ 1.0 & 1.0 & 1.0 & 10.85 \end{pmatrix}$$

The results of the diagonalization must be corrected by adding -0.40 eV [1], which is confirmed by applying Equation (1). The following eigenvalues are then obtained for carbazole: 7.83, 8.16, 8.83, 9.42, 10.95, 11.12 and 13.36 eV.

This leads to the following assignment: π_3 -ionization at 10.79 eV, π_2 at 11.3 eV and π_1 at 13.5 eV (Figure 4).

In the case of dibenzofuran the results of the matrix diagonalization are: 8.23, 8.87, 9.23, 9.96, 11.35, 12.37 and 14.22 eV with a negligible inductive effect of oxygen which is also confirmed by applying

Equation (1). This helps to assign the \tilde{D} system at 11.21 eV to π_3 -ionization indicating the systems at about 11.5 eV as σ -onset. The π_1 - and π_2 -ionizations should then be expected around 12.1 and 14.5 eV, respectively (Figure 5).

Dibenzothiophene and Phenanthrene

The PE spectrum of dibenzothiophene (Fig. 6) shows that it fits into the group of fluorene analogues; thus it is reasonable to expect the top five systems to arise from π -ionizations. This expectation is supported by the HMO calculation. However, the results of the matrix procedure similar to that applied to carbazole and dibenzofuran by simply using the H_2S lone-pair ionization at 10.48 eV [14] show poor agreement with the experimental results. Further support for a proper assignment, however, can be taken from the PE spectrum of the compound investigated next, namely phenanthrene. The PE spectrum of phenanthrene (Fig. 7) is very similar to that of dibenzothiophene, especially in the low energy region. The main differences are within the system at 11.03 eV in the former, which can be attributed to π -ionizations mainly localized on C–H bonds at position 9 and 10. Earlier assignments on phenanthrene agree that the top four systems arise from π -ionizations [15, 16]. The simple matrix procedure for phenanthrene performed in the same manner as for the other fluorene analogues with the π -ionizations for ethylene at 10.51 eV [14] does not produce so satisfactory results. Thus, it appears that

possibly symmetry reasons applied to the exclusion of the π_2 , π_5 , and π_6 orbitals of the planar biphenyl do not hold for phenanthrene. A possible explanation here is that the energy values used for the heteroatoms or groups represent the energies of states, which appreciably include the lowest unoccupied orbitals, particularly if the HOMO-LUMO gap is relatively small. This indeed is the case for ethylene; moreover, the π -antibonding orbital is antisymmetric to the plane separating the two benzene units in planar biphenyl. However, the π_2 , π_5 and π_6 -ionizations should be discriminated by taking the value of interacting off-diagonal elements somewhat smaller, e.g. only half of the original value. A similar reasoning is valid for the sulphur heteroatom where the unoccupied antisymmetric 3d orbitals are only a few electronvolts higher than the occupied 3p orbital. This leads to the following matrix for phenanthrene:

$$\begin{pmatrix} 8.23 & 0 & 0 & 0 & 0 & 0.5 \\ 0 & 9.23 & 0 & 0 & 0 & 1.0 \\ 0 & 0 & 9.23 & 0 & 0 & 0.5 \\ 0 & 0 & 0 & 10.23 & 0 & 1.0 \\ 0 & 0 & 0 & 0 & 11.35 & 0.5 \\ 0 & 0 & 0 & 0 & 0 & 13.35 \\ 0.5 & 1.0 & 1.0 & 1.0 & 0.5 & 1.0 & 10.51 \end{pmatrix}$$

with the following eigenvalues: 7.95, 8.55, 9.23, 9.82, 11.08, 11.75 and 13.75 eV. For dibenzothiophene the results are 7.94, 8.56, 9.23, 9.82, 11.08, 11.74 and 13.74 eV. The results indicate the following assignment for phenanthrene: 7.85 eV (π_7), 8.28 eV (π_6), 9.25 eV (π_5), 9.85 eV (π_4),

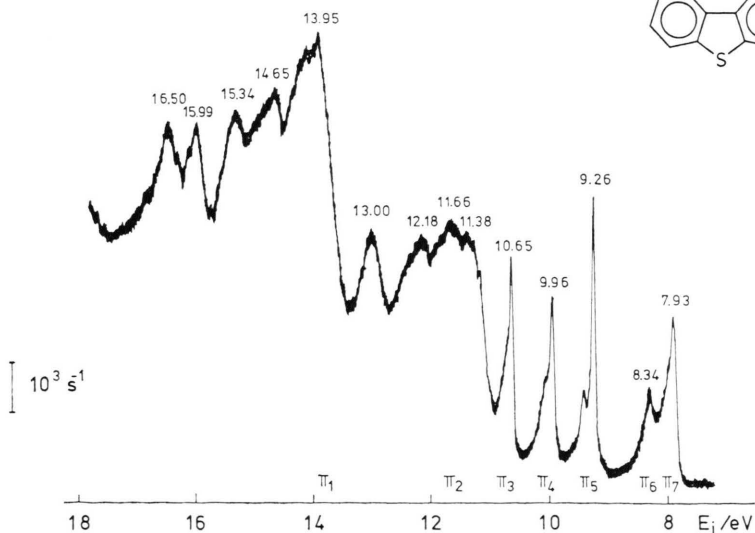


Fig. 6. He(I) photoelectron spectrum of dibenzothiophene.

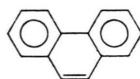
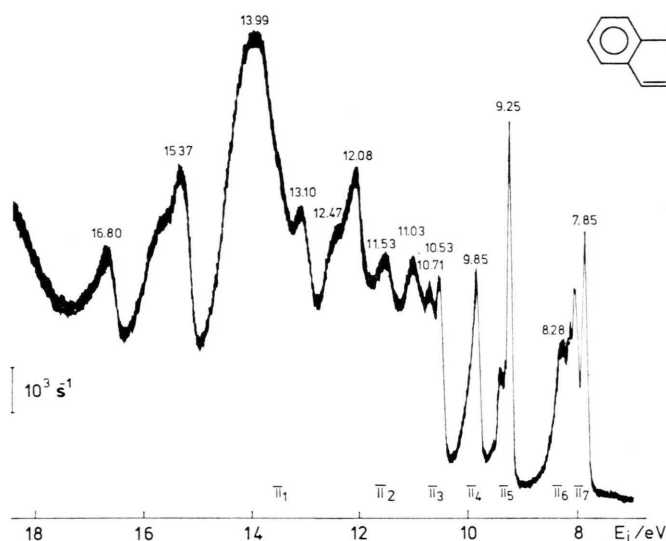
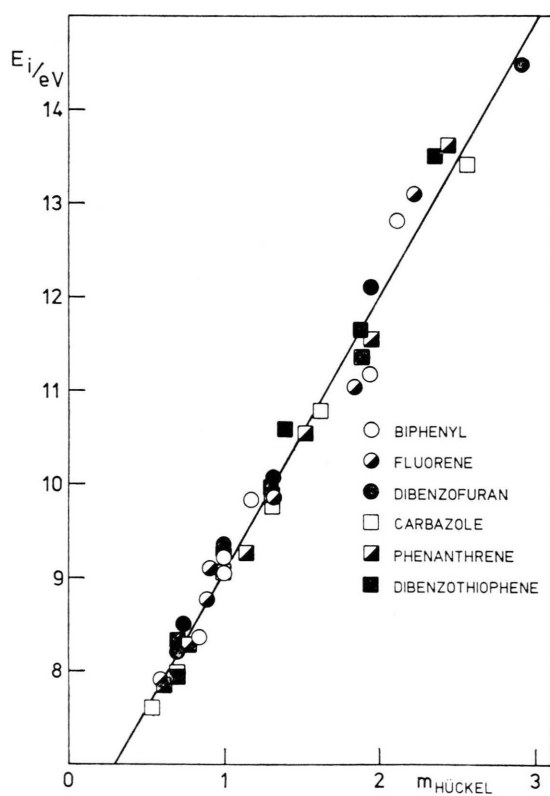


Fig. 7. He(I) photoelectron spectrum of phenanthrene.

Fig. 8. Least squares regression of the π -ionization energies assigned vs. results of HMO calculations for fluorene analogues.

10.53 eV (π_3), 11.03 eV (σ -onset), 11.53 eV (π_2), and ~ 14.0 eV (π_1) (see Figure 7). This assignment is also supported by the HMO results (see Figure 8). The similarity of the behaviour of a sulphur heteroatom and a carbon-carbon double bond, as far as orbital energies are concerned [17], now allows an analogous assignment for the π -ionization energies of dibenzothiophene (see Figure 6).

The correction of the inductive effect for dibenzothiophene according to Eq. (1) gives a very low inductive effect for sulphur, in any case not greater than 0.1 eV.

An interesting consequence of the matrix interaction procedure is the insight obtained into the behaviour of the highest energy π -ionization (π_1) of the molecule investigated. Thus, the energy of the π_1 -ionization in benzene is 12.35 eV, in planar biphenyl 13.35 eV, and in any further interaction this ionization energy can only be enhanced. This means that one should not be tempted to assign the system at 13.10 eV in phenanthrene or 13.00 eV in dibenzothiophene to ionization from the π_1 orbital. Such assignment would presumably predict the energy too low.

A least squares regression of the π -ionizations observed versus the HMO results for the fluorene analogues (Fig. 8) furnishes the following values for the Coulomb and resonance integrals:

$$\alpha_c = 6.14 \pm 0.14,$$

$$\beta_{cc} = 2.93 \pm 0.08,$$

and agrees well with those quoted previously [1, 18].

The interaction matrix method described is quite simple; nevertheless, the results agree with the experimental values within an error of a few percent. This procedure, in connection with HMO calculations, represents a useful help in the interpretation of PE spectra.

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