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Molecular fragment approach to the study of pyrrole oligomers and polypyrrole

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Abstract. A molecular fragment approach is used to compute ionization potentials, transition energies and electron affinities of pyrrole oligomers. The calculations of these quantities include correlation energy contributions evaluated by integrating a functional of the two-particle Hartree-Fock density matrix. Pyrrole oligomers with chains of up to 16 rings are explicitly treated and the calculated quantities extrapolated to the limit of an infinitely long chain, to predict polymer properties. The theoretical results compare favorably with data on gas-phase ionization potentials deduced from experimental oxidation potentials, and with optical absorption peaks recorded in solution or on solid films. The large discrepancy between electron affinities obtained from the eigenvalues of an independent-particle frozen-orbital calculation and those obtained from separate, correlated calculations on the neutral system and the negative ion in shown.

Key words: Pyrrole oligomers – Polypyrrole – Molecular fragment calculations – Ionization potentials – Electron affinities – Transition energies

1 Introduction

Heterocyclic conjugated polymers are still a major area of interest, both in applied and theoretical chemistry, because of several important properties. They become electrically conducting when doped and still maintain the attractive chemical and mechanical features of the polymers [1–5]. They usually present fast and large nonlinear optical responses [6–9] which make them interesting for the development of laser technology and information-storage devices. Some of these materials are electroluminescent under appropriate conditions [10], a fact that has opened a whole new branch of material science focused on the so called organic light-emitting diodes and devices.

Theoretical investigations of these systems can help to find microscopic explanations of macroscopic properties, and give useful information to experimentalists looking for means of synthesizing new materials with improved properties. It is of special interest to study the electronic properties of these polymers – in their neutral and charged states – since these properties are directly related to the electric conductivity, ionization potentials (IP), optical transition energies, electron affinities (EA) redox potentials and other quantities that can be either directly measured or deduced from experimental data.

A characteristic feature of the heterocyclic conjugated polymers, like polypyrrole, polythiophene, and polyfurane, is the relatively small number of monomers in their chains, less than 50, for example, in the case of the polypyrrole. This suggests that a suitable approach to study these polymers is through the analysis and extrapolation of the properties of the corresponding oligomers. One observes, indeed, both from the experimental data and from different types of calculations [11–21], that several of these properties show a dependence on the chain length which can be rationalized in terms of simple analytic functions of the number of monomers in the chain. The results of the extrapolations of the calculated quantities, however, strongly depend on the quality of the calculations carried out on the separate oligomers and on the length of the chains that have been actually treated. On the other hand, the computational effort necessary to perform all-electron calculations on large systems increases so rapidly with the number of atoms that a sophisticated computational network is required when studying relalistic polymeric chains. One of the aims of this paper is to show that non-empirical Hartree-Fock (HF) plus correlation energy calculations can be efficiently and accurately performed on a standard workstation also for oligomers with chains on the order of twenty monomers of pyrrole type. By exploiting this fact, one can make realistic extrapolations of the properties calculated for the oligomers toward the limit of a real polymeric chain and, thus, obtain reasonable estimates of corresponding properties of real systems.

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The simplification of the computational procedures is achieved by exploiting the chemical features of these systems as a guide to set up appropriate, chemically well defined approximations in the framework of a rigorous ab initio approach. The chosen method is the molecular fragment approach (MFA), recently proposed by the authors to perform efficient calculations on large systems with a controlled degree of accuracy and without the use of empirical parameters, [22, 23].

Up to now ab initio calculations of five-membered heterocyclic oligomers have been performed only on oligomers ranging from the monomer to the pentamer [15, 16] and excited states have been calculated only for mono- and bi-pyrroles [20]. The quality of such calculations decreases rapidly with the increase of the size of the oligomers, both as regards the basis set used for the orbital representation and the amount of correlation energy included.

Semiempirical quantum-chemical treatments [17, 20, 21] and approaches based on effective Hamiltonians, like the so called valence effective Hamiltonian (VEH), [11–13, 18, 19], have been widely used to study both polymers and oligomers. The results obtained from semiempirical methods, however, strongly depend on the type and extension of the chosen parametrization, as shown also by the examples reported in Sect. 3. The use of these techniques is, thus, really justified only when other approaches, without empirical parameters, are too expensive. On the other hand, a method like VEH mimics an HF calculation with a set of parametrized one-electron atomic potentials adjusted to give the correct HF results in the case of specific small molecules. We observe, however, that no information pertaining to excited states is included in the atomic potentials, neither are correlation energy contributions taken into account, although this quantity can be important for the evaluation of the energy differences.

In this paper we present the results of calculations performed using jointly the MFA to obtain HF wavefunctions and the CS functional [24–26] of the two-particle HF density matrix to evaluate the correlation energy. The global approach is applied not only to the ground state, but also to excited and ionic states of pyrrole oligomers through a specific variational optimization of the states of interest. This method allows one to obtain realistic and homogeneous values of IP excitation energies, and EA for pyrrole oligomers ranging from the monomer to the 16-pyrrole. The calculated properties are compared with the available experimental data and extrapolated with a linear dependence on the inverse chain length to evaluate the corresponding quantities in the polymer.

The outline of this paper is the following. In Sect. 2 we give a summary of the method used to calculate excitation energies, IP and EA on a sequence of pyrrole oligomers ranging from the monomer to the oligomer with 16 rings. In Sect. 3 we discuss the results of these calculations and their extrapolations to estimate properties of the polymer, and we make a detailed comparison with experimental data and results of other calculations.

2 Molecular Fragment Approach

In this section we summarize the main characteristics of the MFA when applied to pyrrole oligomers in their configuration of minimum energy: a regular and planar chain of $(\alpha - \alpha')$ trans-dipyrrole units. More details of this method, that is based on the use of group functions [27] chosen as suggested by the specific chemical features of the system, can be found in Refs. [22, 23].

Because of the planarity of the pyrrole chains the natural and simplest partition of the electrons is between two groups: one for the σ-electrons localized along the backbone of the chain, and the other for the π-electrons delocalized in the region outside the plane of the chain. These two groups can be described by strong orthogonal group functions, well separated in energy, that give the following exact partition of the total electronic energy:

$$E = E_\sigma + E_\pi \ . \tag{1}$$

The first contribution on the righthand side of Eq. (1) depends on the σ-group function, while E_π represents the energy of the π-electrons in the field of the nuclei and the σ-electrons. This part of the energy, which is strongly modified by excitation or ionization processes involving π-electrons, represents the target of our variational calculations for several different states. In contrast, as regards E_σ, this part of the energy is only slightly modified by perturbing the π-electrons, and, thus, can be treated as a constant shift of the various energies of interest. Similarly, the effective potential due to the σ-electrons is only slightly modified by going from the ground to excited or ionic states of the π-electron system. Therefore, this potential can be represented exactly in the same way both for the excited and ionic states of interest as well as for the ground states of the various oligomers. Finally, we point out that in our approach one can usually choose among different electronic partitions suggested by the chemical features of the system. For example, in our case, the σ-electrons could be partitioned between core-electrons and electrons involved in the σ-bonds. These last could be described by group functions included in the variational procedures, thus achieving a greater flexibility and, therefore, better results with, however, a larger computational effort.

Let us consider now the application of MFA to the study of pyrrole oligomers performed at the HF level of approximation, i.e., with group functions represented by orthonormal spinorbitals obtained via minimization of the following functional

$$E_\pi = \sum_{j=1}^{n_\pi} f_j \langle \varphi_j | \hat{h}' + \hat{G}_\pi | \varphi_j \rangle ; \quad \hat{h}' = \hat{h} + \hat{G}_\sigma \ . \tag{2}$$

In Eq. (2) f_j is the occupation number of the jth orbital, $\hat{h}$ the usual monoelectronic operator and $\hat{G}_{\sigma,\pi}$ the effective potentials due, respectively, to the σ- and π-electrons. These potentials are given in terms of standard Coulomb $(\hat{J}_j)$ and exchange $(\hat{K}_j)$ operators as follows

$$\hat{G}_\sigma = \sum_{j=1}^{n_\sigma}(2\hat{J}_j - \hat{K}_j); \quad \hat{G}_\pi = \sum_{j=1}^{n_\pi}(a_j\hat{J}_j - b_j\hat{K}_j) \tag{3}$$

where the occupation numbers (f_j, a_j, b_j) have been introduced to account for the open shell structure of the excited and ionic states. On the other hand, since the σ-electrons are in a closed shell structure, the σ-orbitals can always be localized through appropriate linear combinations that do not change the energy [28, 29]. It follows that $\hat{G}_\sigma$ can be written as a sum of fragment contributions that, for the pyrrole oligomers, are of three different types: terminal ring, central ring, and interring C—C bond. The corresponding fragment potentials can be split into a short-range part, that is directly transferable among different oligomers, and a Coulomb tail that can be eliminated by adding to each fragment an appropriate charge distribution.

The MFA is a technique that allows one to set up an accurate, non-local representation of the short-range part of the fragment potential after a preliminary localization of the fragment orbitals. In particular, in our case one can write

$$\hat{G}_\sigma = \sum_f \hat{G}^f_\sigma \simeq \sum_f [\hat{g}_f + \hat{v}_f] \tag{4}$$

where

$$\hat{g}_f = \sum_{ij}^{m} |\chi^f_i > g^f_{if} < \chi^f_j|; \quad v_f(\vec{r}) = \sum_\mu \frac{Z^f_\mu}{|\vec{r} - \vec{R}^f_\mu|}$$

$$g^f_{ij} = \sum_{\alpha\beta}^{m} S^{-1}_{i\alpha} \langle \chi^f_\alpha | \hat{G}^f_\sigma - \hat{v}_f | \chi^f_\beta \rangle S^{-1}_{\beta j}; \quad S_{i\alpha} = \langle \chi^f_i | \chi^f_\alpha \rangle \tag{5}$$

and $\{\chi^f_i\}$ is the set of basis functions used to represent the effective potential of the fragment f on which they are localized. The Coulomb tail of the fragment potential is cancelled by $\hat{v}_f$, a damping potential given in terms of effective charges $\{Z^f_\mu\}$ localized on appropriate positions $\{\vec{R}^f_\mu\}$ in the fragment region. Each damping potential $\hat{v}_f$ is added to the standard monoelectronic operator $\hat{h}$ in Eq. (2), and modifies the nuclear potential. The quality of the representation depends on the choice of the basis functions and the type of damping potential used in Eq. (5).

We observe that MFA is based on the chemical separability of one or a few groups of electrons from the sea of the other electrons. This separability does not mean necessarily that the group functions of interest have to be automatically strongly orthogonal to the other groups because of symmetry reasons, as in our case. Small deviations from planarity, for example, maintain the chemical identity of the π-electrons in the pyrrole chains, but introduce an orthogonality potential of the Phillips-Kleimann type [30, 31] that is added to the G_σ potential and can be represented in the same way as G_σ.

In what follows we give the details of a few prototype calculations performed on the first four pyrrole oligomers, for which the comparison with ab initio calculations can be easily done.

2.1 Computational details

The calculations have been performed using a basis set of Slater functions which assure both the correct cusp behavior of the orbitals on the nuclei and the asymptotic exponential decay of the orbitals' tails. Types of functions and orbital exponents are the following

$[\mathrm{N} : 1s(6.67), 2s(1.95), 2p_\sigma(3.40, 1.95), 2p_\pi(3.40, 1.95, 1.10)]$
$[\mathrm{C} : 1s(5.67), 2s(1.72), 2p_\sigma(3.00, 1.72), 2p_\pi(3.00, 1.72, 1.00)]$
$[\mathrm{H} : 1s(1.20)]$
[Center of rings: $2p_\pi(0.45)$].

Since we are interested only in the pattern of the π-levels, we have chosen a basis set that gives a single-zeta representation of the σ-orbitals and a triple-zeta one of the π-orbitals. The inclusion of a diffuse function on the center of each pyrrole ring is important for the correct representation of the excited singlet and the ground states of the negative ions, expecially for the first three pyrrole oligomers, as will be shown in Sect. 3. The orbital exponent of the diffuse function has been optimized through the analysis of the results for the pyrrole monomer.

The choice of a relatively small set of basis functions on each monomer is also intended to show that even this set is sufficient, within our approach, to perform a quantitative analysis of several electronic properties of such systems, with results that compare favorably with the experimental data. Finally, we point out that, by enlarging progressively the basis set used to represent the effective G_σ potential, the MFA energies converge progressively to the corresponding HF energies calculated with frozen σ-orbitals – see, e.g., Refs. [22, 23].

In the present calculations we have used the same structural parameters for all the oligomers and the states of interest. Bond lengths and bond angles are those of Ref. [32] obtained by averaging the X-ray diffraction data of crystalline bi- and tri-pyrroles. The effective potential $\hat{G}_\sigma$ has been obtained using the results of an all-electron HF calculation on the 4-pyrrole, followed by the localization of the σ-orbitals with the Boys method [29]. Each $(g_f + v_f)$ matrix has been built up in such a way as to reproduce the matrix elements of $\hat{G}^f_\sigma$ between $2p_\pi$ functions belonging to the basis set centered on the fragment itself and on the neighboring fragments up to the second nearest neighbor.

The effective potential used to cancel the Coulomb tail of a given $\hat{G}^f_\sigma$ has been built up as follows. For any given σ-orbital, localized between two nuclei A and B of the fragment f, we have added to A and B the following negative charges in atomic units: $q_\mathrm{A} = -b/d$, $q_\mathrm{B} = -a/d$, where $d = a + b$ is the internuclear distance and a and b the distances of A and B from the center of the orbital charge distribution. More sophisticated procedures can be used to prepare each damping potential – see, e.g., Ref. [23] – but the chosen approach, although very simple, guarantees accurate values of the HF orbital energies. We observe that these preliminary procedures, necessary to implement the MFA, require only the analysis of the results of all-electron HF calculations performed on the ground state of the prototype molecules. They constitute the analog of the preliminary calibration of the empirical parameters in a standard semiempirical technique, and can be implemented very easily and with the chosen degree of accuracy.

In Table 1 we compare various energy differences evaluated both with MFA and with standard all-electron HF calculations performed using the above basis set without the diffuse function on the center of each pyrrole ring. As one can see, the distance between the corresponding values obtained from the two methods is, at most, on the order of 0.4 eV and decreases rapidly with the number of rings in the chain.

In Table 2 we compare the efficiency of an MFA calculation with that of a standard all-electron calculation, considering both the time for the integrals and that for a single SCF cycle. These values show that MFA is more than 40 times faster than an all-electron calculation in the integral evaluation, and about 20 times faster in each SCF cycle. The savings in computational time is thus comparable to that of a standard semiempirical method.

Finally, for the evaluation of the correlation energy via the CS functional [24–26] we have used procedures analogous to those explained in Ref. [26]. Our all-electron calculations show that the average values of correlation energy per ring and per state are already stabilized with a chain of four pyrrole rings. These values can therefore be used to estimate the correlation energies also for the states of the other pyrrole oligomers.

3 Results and discussion

The results obtained from our calculations are summarized in Tables 3 and 4. For the first four pyrrole oligomers the reported values are those obtained from relaxed all-electron calculations, while for the other oligomers the results are those of the MFA.

Let us consider first the gas-phase IP. In Table 3 we compare the results of semiempirical and VEH calculations with our results, which are differences between the ground state energies of the singly ionized and neutral system calculated without and with the inclusion of the correlation energy. For the monomer the calculated value is compared with the IP measured in a gas-phase photoemission experiment [21], while for the bi- and tri-pyrroles and for the polymer our data are compared with the IP deduced from oxidation potentials measured with respect to a saturated calomel electrode (SCE) [12]. Following the procedures of Ref. [12] we have added to the measured oxidation potentials two contributions: a polarization energy correction due to solid state effects (estimated at between 1.5 and 2.0 eV Ref. [33]) and a scale factor relating SCE to vacuum (estimated at between 4.4 and 4.7 eV, Ref. [12]). The results of this procedure are the upper and lower limits reported in the last column of Table 3. Note that the same procedure, when applied to the monomer, gives an IP between 7.2 and 8.0 eV, therefore an upper limit that is 0.2 eV below the IP obtained from the gas-phase photoemission experiment. This indicates, first, that the upper limits are probably more realistic, second, that the oxidation potentials are probably underestimated due to the non-reversibility of the oligomer oxidation [12].

The results in Table 3 show that the VEH values for the oligomers are close to our SCF IP (about 0.1 eV higher), apart from the monomer where the difference is about 0.4 eV. Inclusion of the correlation energy increases all the SCF IP by about 0.9 eV, and the correlated values are about 0.4 eV higher than the upper limit of the corresponding experimental value. This nearly uniform shift is mainly due to the use of a poor representaion of the σ-skeleton in terms of frozen σ-orbitals. A linear interpolation of the correlated results with the inverse of the number, n, of pyrrole monomers in the chain is quite satisfactory for $n \geq 3$ (correlation factor 0.9937), and gives a value for the polymer of 5.91 eV. If also the first two oligomers are included in the linear interpolation then the correlation factor reduces to 0.9546 and the extrapolated value for the polymer becomes 6.15 eV. Both these values are consistent with the upper limit of the experimental IP for the polymer and are close to the greater value obtained from VEH calculations.

Other oxidation potentials, measured with respect to a Ag/Ag$^+$ electrode, have been recently published for pyrrole oligomers with up to seven rings [34]. These data vary in a linear fashion with the inverse of the degree of oligomerization (correlation factor 0.9981), but the slope is approximately half that obtained from the linear extrapolation of our calculated values. A similar result has been obtained also in Ref. [12], where the slope of the VEH IP is compared to that of the measured oxidation potentials, both reported as linear functions of $1/n$. This discrepancy can be probably attributed to the fact that the solid state polarization correction changes with the number of monomers in the chain.

Table 1. Comparison of Hartree Fock (HF) energy differences obtained from all-electron (AE) and molecular fragment approach (MFA) calculations and given as functions of the number (n) of monomers in the pyrrole chain. All quantities in eV

n	Singlet		Triplet		Cation		Anion	
	AE	MFA	AE	MFA	AE	MFA	AE	MFA
1	7.61	7.65	3.83	3.92	7.71	8.15	−3.95	−4.20
2	5.75	5.79	3.63	3.68	6.69	6.93	−2.56	−2.74
3	5.06	4.98	3.16	3.15	6.13	6.22	−2.04	−2.17
4	4.76	4.69	3.12	3.11	5.85	5.82	−1.77	−1.87

Finally, to point out the relevant differences that can be found using different semiempirical methods, we have reported, in the second and third columns of Table 3, the INDO and MNDO ionization potentials obtained from the corresponding HOMO energies. We see that the MNDO values are higher than the corresponding INDO IP, with a difference that increases from 1 eV to about 1.4 eV with increasing length of the pyrrole chain.

Let us consider now the optical gaps (E_g), i.e., the excitation energies to the first optically allowed singlet state. The results reported in Table 4 show that the MNDO values, obtained as LUMO-HOMO energy differences, are about 3.5–4 eV higher than the experimental values. This overestimation of the optical gaps when evaluated from the LUMO-HOMO energy differences is characteristic of both semiempirical (see also INDO/SCF gaps [17]) and ab initio HF calculations. Only the VEH results obtained through these differences are sufficiently close to the experimental values. There is no definite explanation of this fact, but only arguments relative to the way in which the effective potential has been parametrized [11, 12]. Note that a small CI performed inside the INDO scheme gives values appreciably lower (third column of Table 4) than those obtained from INDO/SCF calculations. These values do not change appreciably with a multireference, CI, i.e. starting from a many configuration reference state (fourth column of Table 4). We point out, however, that the results of small CI calculations are strongly dependent on the type and number of included configurations.

Our results show that the energy gap calculated for the pyrrole monomer is very sensitive, as expected, to the inclusion of a diffuse $2p_\pi$ function on the center of the pyrrole ring. The diffuse function lowers the SCF E_g by about 1.8 eV, but this change is partially compensated by the decrease, in absolute value, of the correlation energy of the excited state. Both these effects are due to the fact that the diffuse function gives a Rydberg character to the HF wavefunction of the excited singlet state.

Table 2. Ratio between the time needed for integral evaluation in MFA (t^{I}_{M}) and the corresponding time in an all-electron HF calculation (t^{I}_{A}) as a function of the number of monomers in the pyrrole chain; the same for the time needed for an SCF cycle in MFA (t^{S}_{M}) and the corresponding time in an all-electron HF calculation (t^{S}_{A})

n	$(t^{I}_{M}/t^{I}_{A}) \cdot 100$	$(t^{S}_{M}/t^{S}_{A}) \cdot 100$
1	4.8	15.3
2	3.2	10.5
3	2.4	7.1
4	2.3	5.9

Table 3. Gas-phase first IP as a function of the number of pyrrole rings in the chain. INDO and MNDO values from Refs. [12, 17], VEH values from Refs. [12, 13, 19], ground state energy differences between the singly ionized and neutral system calculated without (Δ_{HF}) and with (Δ_{CS}) the inclusion of the correlation energy. The experimental IP have been obtained from a gas-phase photoemission experiment for the monomer [21] and from measured oxidation potentials [12] for the oligomers and the polymer. All quantities in eV

n	INDO	MNDO	VEH	Δ_{HF}	Δ_{CS}	Expt
1	–	8.57	8.13	7.70	8.60	8.23
2	6.89	7.86	6.89	6.79	7.67	6.4 – 7.3
3	–	7.59	6.43	6.30	7.37	6.1–7.0
4	6.27	7.47	–	6.02	6.90	–
6	6.09	7.36	–	5.72	6.60	–
10	5.97	7.31	–	5.45	6.34	–
12	–	–	–	5.38	6.26	–
14	–	–	–	5.33	6.22	–
16	–	–	–	5.30	6.18	–
∞	–	7.10	5.68–5.83	–	–	5.3–6.3

Table 4. Energy gaps E_g as a function of the number of pyrrole rings in the chain. INDO/CI (labelled ICI) and MNDO values from Refs. [12, 17], INDO/MRD-CI (labelled IMR) from Ref. [22], VEH values from Refs. [12, 13, 19], transition energies calculated without (Δ_{HF}) and with (Δ_{CS}) the inclusion of the correlation energy (value in parentheses calculated without diffuse functions). The experimental values have been obtained from the maximum of the optical absorption peaks in acetonitrile [32] the second value of E_g for the polymer (3, 2) is taken from Ref. [21]. All quantities in eV

n	MNDO	ICI	IMR	VEH	Δ_{HF}	Δ_{CS}	Expt.
1	–	–	5.44	7.01	5.84 (7.61)	6.59 (7.45)	5.96
2	8.25	3.91	3.77	5.24	5.32 (5.75)	6.00 (5.70)	4.49
3	–	–	3.32	4.35	5.19 (5.06)	5.80 (5.00)	3.91
4	7.35	3.02	3.02	–	5.02	5.56	–
5	–	–	2.88	–	4.87	5.34	3.38
6	7.07	2.73	2.79	–	4.75	5.15	–
7	–	–	–	–	4.65	4.98	3.25
10	6.90	2.54	–	–	4.44	4.57	–
12	–	–	–	–	4.34	4.34	–
14	–	–	–	–	4.27	4.27	–
16	–	–	–	–	4.22	4.22	–
∞	6.52	2.17	–	2.99–4.0	–	–	2.8–3.2

The correlated value of E_g is approximately 0.7 eV higher than the experimental one, a difference that is probably due to the poor representation of the σ-skeleton. As expected, in the case of the bi- and tri- pyrroles the diffuse functions contribute significantly less than in the case of the monomer, since the cooperative effects of the basis functions on different rings already allow a partial delocalization of the excited electron along the chain. Also the correlation energy contribution to the energy gap decreases progressively with the increase of the chain length, since the difference between the electronic densities of the excited singlet and the ground state reduces progressively. We observe, however, that the difference between calculated and experimental values is larger for oligomers than for the monomer. This is probably due to the fact that the optical spectra have been recorded in condensed phase, where the optimal ground state configuration of the oligomers can be slightly distorted from planarity and such a distortion can appreciably lower the optical gap.

If plotted as a function of the inverse number of pyrrole rings in the chain, the curve of the optical gaps, calculated including the correlation energy, is nearly linear for $n \geq 3$ (correlation factor 0.9405), and gives for the polymer a value of 3.93 eV. It is not surprising that the estimated gap for the polymer is about 0.7 eV above the highest experimental value, since our calculations have been performed for planar and regular structures of isolated pyrrole chains. Effects due to the chemical and structural disorder, which cause differences up to 0.4 eV between absorption peaks measured on differently prepared polypyrrole samples, have thus been completely disregarded. Furthermore, it is known that the relaxation effects due to the environment of the polymeric chains in solution or solid films shift the optical gaps higher by approximately 0.1–0.2 eV for an isolated chain [21, 35].

Table 5. Transition energies to the first excited state (a triplet) calculated with the inclusion of the correlation energy and given as a function of the number of pyrrole rings in the chain. All quantities in eV

n	Δ_T
1	3.99
2	3.74
3	3.52
4	3.36
6	3.24
10	3.14
12	3.11
14	3.09
16	3.07
∞	–

In Table 5 we report the transition energies to the lowest excited state (a triplet) of each pyrrole oligomer, calculated including the correlation energy. The triplet state cannot be appreciably populated via direct optical transitions, but can be reached through different mechanisms, e.g., decay processes from higher excited states coupled to the triplet by matrix elements of the relativistic Hamiltonian. It is interesting to note that these excitation energies approach from below the corresponding experimental optical gap, being about 2 eV lower in the case of the monomer and almost equal in the case of the polymer. Indeed, if plotted as a function of the inverse number of pyrrole rings in the chain, the curve of these excitation energies is nearly linear for $n \geq 3$ (correlation factor 0.9976), and gives a value for the polymer of 2.97 eV. If also the first two oligomers are included in the linear interpolation, the correlation factor decreases to 0.9308 and the lowest excitation energy for the polymer becomes 3.07 eV.

Let us consider now the EA defined as the IP of the negative ion. In Table 6 we report the electron affinities estimated from INDO and MNDO calculations [17] using the expression: $\mathrm{EA} = -\epsilon_{\mathrm{LUMO}}$, and the VEH values obtained from the relationship $\mathrm{EA} = \mathrm{IP} - E_g$. Both these expressions give an estimate of the EA in the HF approximation while neglecting the differences between orbitals of the neutral system and the negative ion. We see that INDO and MNDO predict small EA values, while VEH gives exceedingly large EA. Note that values greater than 1.5 eV are characteristic of radicals or molecules with electronegative substituents like the halogens [36].

Our SCF calculations predict a large instability of the negative ions, i.e., the EA is zero both for the oligomers and for the polymer. These results are strongly sensitive to the inclusion of a diffuse function on the center of each pyrrole ring, which drastically lowers the absolute

Table 6. EA values as a function of the number of pyrrole rings in the chain. INDO and MNDO values from Ref. [17], VEH values evaluated as $\mathrm{EA} = \mathrm{IP} - E_g$ from Tables 2 and 3, energy differences between neutral system and negative ion calculated without (Δ_{HF}) and with (Δ_{CS}) the inclusion of the correlation energy (values in parentheses calculated without diffuse functions). All quantities in eV

n	INDO	MNDO	VEH	Δ_{SCF}	Δ_{CS}
1	–	–	1.12	−1.72 (−3.95)	−1.60 (−3.11)
2	−0.34	−0.39	1.65	−1.63 (−2.56)	−1.50 (−1.74)
3	–	–	2.08	−1.56 (−2.04)	−1.41 (−1.17)
4	0.17	0.12	–	−1.51	−1.34
6	0.34	0.29	–	−1.45	−1.25
10	0.45	0.14	–	−1.39	−1.12
12	–	–	–	−1.37	−1.08
14	–	–	–	−1.36	−1.03
16	–	–	–	−1.35	−0.99
∞	–	–	1.68–2.84	–	–

values of the energy differences by allowing a better delocalization of the negative charge. This is especially true for the first three pyrrole oligomers, but the effect is reduced when the chain length is increased because of the cooperative effects of the basis functions on different pyrrole rings which already allow a partial delocalization of the negative charge along the chain. The correlation energy lowers the absolute value of the energy differences even further with a contribution that increases slowly, in absolute value, with the chain length, but remains inadequate to stabilize the negative ion.

If plotted against the inverse number of pyrrole rings in the chain, our correlated results show nearly linear behavior for $n \geq 3$ (correlation factor 0.9470). The limiting value for the polymer is negative (−0.94 eV), thus predicting the instability of the negative ion in the polymer. This result is in agreement with the fact that, to our knowledge, no experimental observation of polypyrrole reduction has been reported.

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