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Ionization Potentials and Electron Affinities of Carbo- and Heterocyclic π-Conjugated Molecules

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The correlations of the observed ionization potentials and electron affinities with the orbital energies of SCF-MO's calculated by the variable-β modification of the Pariser-Parr-Pople method were examined for 30 conjugated molecules including heterocycles. A simple linear relation has been found between the ionization potential and the energy of the highest occupied SCF-MO as well as between the electron affinity and the energy of the lowest vacant SCF-MO. The ionization potential and electron affinity are estimated by using these empirical relations for 24 conjugated heteromolecules of biochemical interest.

PPP-Rechnungen nach der variablen β-Methode an 30 carbo- und heterocyclischen π-Systemen zeigen eine gute Korrelation der experimentellen Ionisationspotentiale und Elektronenaffinitäten mit den Energien der höchsten besetzten bzw. tiefsten unbesetzten SCF-MOs. Die so erhaltenen Regressionsgeraden wurden zur Bestimmung von Ionisationspotentialen und Elektronenaffinitäten von 24 biochemisch interessanten Heterosystemen herangezogen.

Examen pour 30 molécules conjuguées des corrélations entre potentiels d'ionisation et affinités électroniques expérimentales avec les énergies des orbitales moléculaires SCF de la méthode de Pariser-Parr-Pople à β variable. Une relation linéaire simple a été trouvée entre le potentiel d'ionisation et l'énergie de la plus haute orbitale moléculaire occupée ainsi qu'entre l'affinité électronique et l'énergie de la plus basse orbitale vacante. Ces relations empiriques permettent d'estimer les potentiels d'ionisation et l'affinité électronique de 24 molécules conjugées d'intérêt biochimique.

Introduction

It has been well established for conjugated hydrocarbons that there is a linear relation between the ionization potential and the energy of the highest occupied molecular orbital calculated by the Hückel theory [1, 2, 3]. A similar correlation is known also between the electron affinity and the energy of the lowest vacant molecular orbital [1]. Therefore the orbital energies of the Hückel molecular orbitals have been often used to predict the electron donor or acceptor properties of conjugated molecules, especially for the complex molecules of biochemical interest [4].

Unfortunately, however, the correlation of the Hückel orbital energy with the ionization potential or with the electron affinity has not been well proved for conjugated molecules containing heteroatoms[1]. In effect, the prediction based on the Hückel orbital energy can be quite deficient as regards the electron donor or acceptor properties of some heteromolecules.

[1] The ionization potentials of several conjugated molecules containing heteroatoms were calculated by the ω-technique of the simple LCAO method [5].

The method of the self-consistent-field molecular orbital (SCF-MO) with the Pariser-Parr-Pople formalism has been successfully used in the calculation of the electronic spectra of conjugated molecules. This method should provide much sound basis for the estimation of the ionization potential and electron affinity. According to Koopmans' theorem, the negative of the orbital energy of the highest occupied molecular orbital (HOMO) calculated with Hartree-Fock approximation should be equal to the ionization potential of the molecule. It has been reported, however, that the π-electron ionization potential thus estimated for a conjugated molecule from the orbital energy of the SCF-MO calculated with the usual approximation of the core integrals is often appreciably larger than the observed ionization potential. The validity of Koopmans' theorem for conjugated hydrocarbons was criticized by Hoyland and Goodman [6], who calculated the ionization potential taking into account the effect of the π-electron removal upon the π- and σ-basis functions as well as that of the reminimization of ionic configuration, and obtained a very good agreement with experiment. This method is, however, considerably laborious and may not be easily applied to complex molecules of biochemical interest. Thus it is still of practical significance to establish a more simple semiempirical procedure to predict the ionization potential and electron affinity of a conjugated molecule. It has been shown by Pople [7, 8] that a fairly good agreement between the calculated and observed ionization potentials is obtainable for conjugated hydrocarbons by adjusting empirically the core parameters. A similar procedure was taken by Sidman [9] in his calculation on quinones, and, recently, by Berthod, Giessner-Prettre and Pullman [10] in the calculation of the electronic properties of the purine and pyrimidine components of nucleic acids.

The variable-β procedure of the semiempirical SCF-MO method within the Pariser-Parr-Pople formalism has been developed by Dewar and Schmeising [11], and later by Nishimoto and Forster [12]. This method seems to be most suited for the calculation of π-electron states of complex molecules since, in this method, we need not specify the precise molecular geometry, such as the alternation of bond length, which is not always exactly known. This method was applied to the calculation of the electronic spectra of conjugated molecules containing heteroatoms as well as those of conjugated hydrocarbons, and gave very satisfactory results. We have also shown that it can be used with success in the calculation of the electronic spectra of non-benzenoid aromatics such as tropone and tropolone [13]. It is the purpose of the present paper to report the correlation found of the orbital energies of the SCF-MO's calculated by this method with the observed ionization potential or electron affinity, and to show the possibility of the theoretical prediction of the ionization potentials and electron affinities of complex molecules. We shall also report the results of the calculation on conjugated molecules of biochemical importance.

Method of SCF-MO Calculation

The orbital energies were calculated by a "variable-β" procedure of semiempirical SCF-MO method within the Pariser-Parr-Pople formalism. The parameters were taken as proposed by Nishimoto and Forster [12]. We used the values given by Hinze and Jaffé [14] for the valence state ionization potentials

of atoms, and the one-center repulsion integrals were approximated by the use of the Pariser-Parr approximation [15], namely as $\gamma_{\mu\mu}=I-A$, where I and A are respectively the valence state ionization potential and the electron affinity of the μ-th atom. The values of these parameters are summarized in Table 1.

Table 1

	I (eV)	$\gamma_{\mu\mu}$ (eV)
C^+	11.16	11.13
N^+	14.12	12.34
N^{++}	26.7	17.44
O^+	17.70	15.23
O^{++}	32.9	21.53

The two center core integrals, $\beta_{\mu\nu}$, were adjusted at each iteration by the use of the relation,

$$\beta_{\mu\nu}=A_0+A_1P_{\mu\nu} \tag{1}$$

where $P_{\mu\nu}$ is the bond order. The values of A_0 and A_1 assumed in the present calculation, are given in Table 2. The two center repulsion integrals, $\gamma_{\mu\nu}$, were kept

Table 2. *Assumed values of A_0 and A_1*

Bond	A_0 (eV)					A_1 (eV)
	n[a]=1	2	3	4	5	
C–C	−2.04	−1.90	−1.84	−1.82	−1.812	−0.51
C–N	−2.24	−2.09	−2.02	−2.00	−1.982	−0.53
C–O	−2.44	−2.27	−2.20	−2.18	−2.172	−0.56

[a] The number of benzene ring in a molecule.

fixed, which were estimated by the use of the Nishimoto-Mataga approximation [16],

$$\gamma_{\mu\nu}=e^2/(a_{\mu\nu}+r_{\mu\nu}) \tag{2}$$

where $r_{\mu\nu}$ is the distance between the two atoms. The constant, $a_{\mu\nu}$, was determined as follows,

$$1/a_{\mu\nu}=(1/a_{\mu\mu}+1/a_{\nu\nu})/2 \tag{3}$$

where $a_{\mu\mu}=e^2/\gamma_{\mu\mu}$.

In the present calculations of SCF-MO's, sufficient self-consistency was attained in most cases after the tenth iteration. All calculations were performed with HITAC 5020 E at the Computer Centre, University of Tokyo.

Results and Discussions

1. The Correlation of the Orbital Energies with the Ionization Potential and Electron Affinity

We examined the correlation of the calculated orbital energy of the highest occupied SCF-MO with the observed ionization potential. The orbital energies

and the available experimental data of ionization potential are summarized in Tables 3, 4, and 5, together with the data of electron affinity.

The ionization potential has been determined for a number of conjugated molecules by means of the photoionization method [17, 18]. These values are known to give the adiabatic ionization potential, and usually coincide well with the ionization potentials determined from the spectroscopic method [19, 20]. On the other hand, the electron impact method [21, 22] gives the non-adiabatic

Table 3. *The ionization potentials and the electron affinities of aromatic hydrocarbons (eV)*

Molecule	Experimental values					Present calculation	
	IP				*EA*[f]		
	Photoionization		Spectro-	Electron	Electron	*IP*	*EA*
	Terenin[a]	Watanabe[b]	scopic[c]	impact	capture		
1 Benzene	9.24	9.245	9.24	9.38[d]	(−0.94)[g]	9.287	−0.057
2 Naphthalene	8.14	8.12		8.26[d]	0.148	8.128	0.102
3 Anthracene	7.38			7.55[d]	0.556	7.588	0.742
4 Tetracene	6.88			6.95[e]	(1.42)[g]	7.094	1.136
5 Pyrene				7.72[e]	0.591	7.489	0.741
6 Perylene						7.211	1.019
7 Phenanthrene				8.03[d]	0.307	8.007	0.223
8 1,2-benzanthracene					0.630	7.569	0.661
9 Triphenylene				8.19[e]	0.285	8.117	0.113
10 Chrysene				8.01[e]	0.397	7.731	0.499
11 Picene					0.542	8.689	0.601
12 1,2,5,6-dibenzanthracene					0.595	7.605	0.625

[a] Reference [18]; – [b] Reference [17]; – [c] Reference [19]; – [d] Reference [21]; – [e] Reference [22]; – [f] Reference [23].

[g] Calculated from the ionization potential *IP* by using the relation $\chi = (IP + EA)/2$, where χ is the molecular electronegativity and its value is taken as 4.15 ± 0.05 eV. See Reference [23].

Table 4. *The ionization potentials and the electron affinities of the derivatives of aromatic hydrocarbons (eV)*

Molecule	Experimental values			Present calculation	
	IP		*EA*[c]	*IP*	*EA*
	Terenin[a]	Watanabe[b]			
13 Phenol	8.52	8.50		8.287	−1.209
14 Aniline	7.69	7.70		7.743	−1.304
15 *p*-benzoquinone	9.68		0.77 (1.37)[d]	9.979	1.944
16 Anthraquinone	9.34		0.5	9.262	1.280
17 1-naphthylamine	7.30			7.309	−0.200
18 2-naphthylamine	7.25			7.459	−0.146
19 Benzaldehyde	9.60			9.453	0.160
20 1,4-naphthoquinone			0.7	9.465	1.602
21 1,2-naphthoquinone			0.6	8.845	1.516
22 1-hydroxy-9,10-anthraquinone			0.7	8.251	1.332
23 Pyromellitic dianhydride			0.85	10.107	1.841
24 Phthalic anhydride			0.15	9.742	0.988
25 Maleic anhydride			0.57	10.248	1.430

[a] Reference [18]; – [b] Reference [17]; – [c] Reference [24]; – [d] Reference [25].

Table 5. *The ionization potentials and the electron affinities of heterocyclic compounds* (eV)

Molecule	Experimental values			Present calculation	
	IP			*IP*	*EA*
	Photoionization		Spectroscopic[c]		
	Terenin[a]	Watanabe[b]			
26 Pyridine	9.40	9.32		9.316	−0.675
27 Quinoline	8.30			8.461	0.361
28 Acridine	7.70			7.879	1.012
29 Furan		8.89	9.05	8.805	−0.643
30 Pyrrole		8.20?	8.90	8.686	−1.877

[a] Reference [18]; – [b] Reference [17]; – [c] Reference [20].

ionization potentials, which are usually a little larger than the ionization potentials given by the other two methods.

In Fig. 1, the observed ionization potential is plotted against the negative of the orbital energy of the highest occupied SCF-MO. As can be seen clearly, all points lie along one straight line of a gradient of unity. This fact means that,

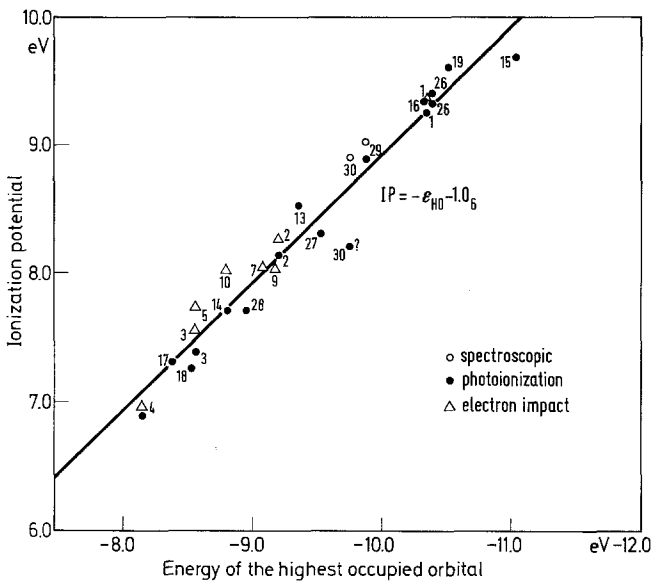

Fig. 1. Correlation between the observed ionization potential and the energy of the highest occupied SCF-MO

although the negative of the orbital energy is not equal to the observed ionization potential, the difference between these two quantities remains constant irrespective of the molecular structure. It should be emphasized here that the data plotted in Fig. 1 include not only those of hydrocarbons but also those of heteromolecules. Thus we can conclude that the correlation of the ionization potential (*IP*) with the orbital energy of the highest occupied molecular orbital (ε_{HOMO}) can be ex-

pressed as follows for hydrocarbons as well as for heteromolecules,

$$IP = -\varepsilon_{\mathrm{HOMO}} - 1.06\,\mathrm{eV}\,. \tag{1}$$

The presence of this simple empirical relation provides us a way to predict the ionization potentials of more complex conjugated molecules by calculating the SCF-MO's with the parameter set assumed in the present study.

The electron affinity is more difficult to determine experimentally as compared with the ionization potential. In effect, an absolute electron affinity has been determined with a sufficient accuracy for non of the conjugated molecules except several hydrocarbons, for which the electron affinity has been recently determined by Becker and Chen [23] from the electron capture method. For several conjugated molecules with heteroatoms, if they behave as the electron acceptor, the electron affinity can be estimated by comparing the wavelengths of the charge-transfer bands for a series of molecular complexes involving a given electron donor. In Table 4, we have given such values of electron affinity proposed by Briegleb [24], who has assumed the electron affinity of *p*-chloranil as 1.37 eV, and used it as the standard.

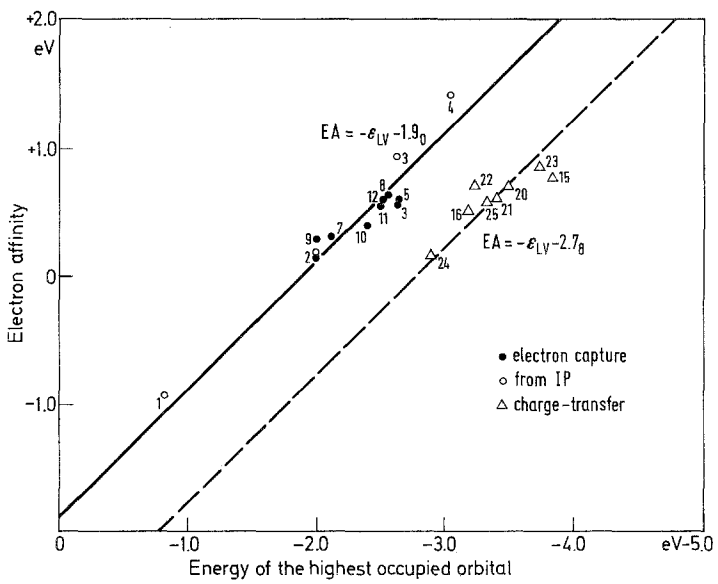

Fig. 2. Correlation between the observed electron affinity and the energy of the lowest vacant SCF-MO

In Fig. 2, we have plotted the electron affinity against the negative of the orbital energy of the lowest vacant molecular orbital calculated by the SCF-MO method. In the case of conjugated hydrocarbons, the correlation can be well described with the following equation,

$$EA = -\varepsilon_{\mathrm{LVMO}} - 1.90\,\mathrm{eV}\,, \tag{2}$$

where EA is the electron affinity and $\varepsilon_{\mathrm{LVMO}}$ is the orbital energy. As shown in Fig. 2, the points of heteromolecules where the Briegleb's values of electron affinity are used, show a systematic deviation from the relation described by Eq. 2.

For the group of these points, the following empirical relation can be given,

$$EA = -\varepsilon_{\mathrm{LVMO}} - 2.78\ \mathrm{eV}\,. \tag{3}$$

It should be noticed, however, that the Briegleb's values of electron affinity are essentially relative ones, and their absolute values are entirely dependent on the assumed electron affinity of *p*-chloranil. Although Briegleb has assumed that the electron affinity of *p*-chloranil is 1.37 eV, Farragher and Page [25] have recently determined it as 2.45 eV by the magnetron method. The same authors have also reported that the electron affinity of *p*-benzoquinone is 1.37 eV, which is 0.6 eV larger than the Briegleb's value. These facts suggest that the Briegleb's values are always 0.6—1.0 eV smaller than the true electron affinities. If we increase them by 0.88 eV, all points in Fig. 2 come to the line corresponding to the correlation given by Eq. 2. Thus it is most likely that Eq. 2 is valid not only for conjugated hydrocarbons but also for heteromolecules. In conclusion it seems possible again to predict the electron affinities of conjugated molecules, with or without hetero-atoms, from the calculated orbital energy by assuming the simple correlation described in Eq. 2.

2. Donor and Acceptor Properties of Conjugated Molecules of Biological Importance

A number of biochemical processes are known to involve an intermolecular electron transfer. Therefore, the ionization potentials and electron affinities of biochemical molecules are of great importance. Unfortunately, however, there is little experimental data on these quantities. Furthermore it is extremely difficult to find any direct experimental method to determine the ionization potential and electron affinity of each tautomeric form of these molecules. Thus, the quantum mechanical predictions on the donor and acceptor properties are of great significance in these cases. Extensive investigations have been carried out primarily by the use of Hückel molecular orbital method [4]. However, the validity of the prediction based on this method is sometimes questionable for heteromolecules as already mentioned. Thus we have calculated the SCF-MO's of these conjugated molecules, and estimated the ionization potential and electron affinity by using the empirical relation described in the preceeding section. The results are given in Table 6 and 7.

The estimated ionization potential is 7—9 eV for most of the purine and pyrimidine derivatives, while the electron affinity is mostly negative with a value in the range of -1.0 to -0.1 eV. This suggests that these molecules are moderately good electron donors, but quite poor acceptors. Alloxane is an exception in this respect. Its ionization potential is as large as 10.77 eV, indicating its very poor ability as an electron donor. It is, however, expected to be a moderately good electron acceptor. We can also conclude that guanine should be the best electron donor among the purine and pyrimidine bases of nucleic acids. These general features of the results of the present calculations are in agreement with the predictions given by the Hückel molecular orbital method [4, 26] except that on the donor property of uric acid. Uric acid has been predicted to be an exceptionally good electron donor from the calculation of Hückel MO's. According to the present calculation, however, its ionization potential is expected to be about

Table 6. *The calculated ionization potentials and electron affinities of purines and pyrimidines (eV)*

	ε_{HOMO}	ε_{LVMO}	*IP*	*EA*
Pyrimidine	−10.77	−1.43	9.71	−0.47
Alloxane	−11.83	−3.56	10.77	1.66
Cytosine				
(lactam, 1-H)	−9.47	−1.66	8.01	−0.24
(lactam, 2-H)	−9.18	−1.66	8.12	−0.24
(lactim)	−9.14	−0.65	8.08	−1.25
Uracil				
(lactam)	−10.22	−1.92	9.16	0.02
(lactim)	−9.48	−0.78	8.42	−1.12
Purine				
(9-H)	−9.95	−1.73	8.89	−0.17
(7-H)	−10.25	−1.80	9.12	−0.10
Adenine				
(9-H)	−9.05	−1.13	7.99	−0.77
(7-H)	−9.32	−1.27	7.26	−0.63
Guanine				
(lactam, 9-H)	−8.72	−0.94	7.66	−0.96
(lactam, 7-H)	−8.92	−0.90	7.86	−1.00
(lactim, 9-H)	−8.63	−0.90	7.57	−1.00
(lactim, 7-H)	−8.76	−1.08	7.70	−0.82
Xanthine				
(lactam, 9-H)	−9.73	−1.23	8.67	−0.66
(lactim, 9-H)	−8.92	−1.00	7.86	−0.90
Hypoxanthine (lactam)	−9.28	−1.58	8.22	−0.32
Uric acid				
(lactam)	−9.51	−1.96	8.45	0.06
(lactim, 9-H)	−9.54	−2.15	8.48	0.25
(lactim : lactam)	−9.53	−2.06	8.47	0.16
2-hydroxypurine	−9.52	−1.99	8.46	0.09
8-hydroxypurine	−9.66	−1.87	8.60	−0.03
2-aminopurine	−8.93	−1.38	7.87	−0.52
8-aminopurine	−8.96	−1.30	7.90	−0.60

Table 7. *The calculated ionization potentials and electron affinities of porphins and poly-pyrroles (eV)*

	ε_{HOMO}	ε_{LVMO}	*IP*	*EA*
Porphin	−8.20	−3.78	7.14	1.88
1,3-divinylporphin	−8.17	−3.82	7.11	1.92
1-vinyl-5-formylporphin	−8.24	−3.82	7.18	1.91
1-vinyl-5,8-diformylporphin	−8.37	−4.03	7.31	2.12
Dipyrrole	−9.18	−3.11	8.12	1.21
Tripyrolle	−9.08	−3.85	8.02	1.95
Tetrapyrrole	−8.95	−4.23	7.89	2.32
Pentapyrrole	−8.90	−4.52	7.84	2.62
Biliverdin				
(keto)	−8.43	−4.04	7.37	2.14
(enol)	−8.29	−3.87	7.23	1.98

8.5 eV in any of its tautomeric forms. Thus it is a relatively poor electron donor even among the purine and pyrimidine derivatives. By studying the charge-transfer bands of molecular complexes which involves tetramethyl uric acid as the electron donor, we have estimated the ionization potential of tetramethyl uric acid as about 7.9 eV. This fact seems to support our prediction mentioned above.

The results of the calculation on porphin and its derivatives, the fundamental skeltons of porphyrins, are given in Table 7, together with those of related compounds, poly-pyrroles. All molecules were assumed to have a planar molecular geometry. For each poly-pyrrole chain there could be several isomelic forms, different in molecular geometry, but we have shown here only the results calculated for the most extended form of each poly-pyrrole chain; the bond angle at the carbon atom between two pyrrole rings is taken as 120°, and the pyrrole ring is assumed as a regular pentagon. In porphine derivatives, the estimated ionization potential is 6.5—7.4 eV and the electron affinity 1.8 – 2.2 eV. This indicates that they are very good electron donor as well as a very good electron acceptor. As compared with these molecules, poly-pyrroles possess, in general, a little higher ionization potential, but their electron affinity are quite large. The electron affinity of penta-pyrrole is expected to be as large as 2.6 eV. It has been predicted by the Hückel method that biliverdin should be an unusually-strong electron acceptor [4], where the lowest vacant molecular orbital possesses the character of a bonding orbital. According to the present calculation, however, there seems to be no reason to expect any unusual acceptor property for this molecule, although it should be a fairly good electron acceptor.

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