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Semi-Empirical Calculations of π-Electron Affinities for Some Conjugated Organic Molecules*

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Energy levels have been calculated for some conjugated systems containing C, N, and O atoms using a semi-empirical *method based upon a* variable β-γ modification of the Pariser-Parr-Pople approximation to the Hartree-Fock equation. Koopmans' theorem is used to relate the calculated energy of the lowest vacant molecular orbital, $\varepsilon_{\mathrm{LVMO}}$, to the adiabatic electron affinity of a molecule. The approach is identical to that used previously by Kunii and Kuroda [13]. An excellent correlation is found between electron affinities deduced from recent beam experiments and $\varepsilon_{\mathrm{LVMO}}$. This relationship is used to predict electron affinities for over 100 other organic molecules. In addition, excited state energies for negative ions are calculated, and good agreement is found with the available experimental data. Bound excited states are also predicted for some organics which contain the $=\mathrm{C(CN)_2}$ substructure. The additive contribution of group substitutions to the electron affinity is discussed for the case of CN substitutions to ethylene, benzene, and naphthalene.

Key word: Conjugated organic molecules, MO levels of ~, ionization potentials of ~, electron affinities of ~

1. Introduction

The electron affinity of a molecule is defined as the difference in energy between the neutral molecule in its ground state, E^0, and the ion in its ground state, E^-, i.e., $EA = E^0 - E^-$. In cases where the ionic surface lies above that of the neutral, a virtual state exists (*negative EA*); and, conversely, when the total energy of the negative ion is below that of the neutral, a bound state exists (positive *EA*). Electron affinity values which have been reported for atoms and small molecules (fewer than 5 atoms) range from approximately -2 eV to $+4$ eV. Studies of electron photodetachment or radiative attachment have provided values for atomic electron affinities with accuracies often less than 10 milli-electron volts (meV). The first accurate halogen electron affinities are credited to Berry and Reimann [1]. There exist very few accurate determinations of molecular electron affinities because of the complexity of molecular negative ions and the inherent difficulties in determining electron affinities. In a few cases (notably NO and O_2) where the photoelectron spectroscopy technique of Hall and associates [2, 3] has been applied, electron affinities are known with accuracies of less than 10 meV. In

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cases where the electron affinity is negative, the resonance scattering technique employed by Schulz and co-workers [4, 5] can provide adiabatic molecular electron affinities with accuracies of about 50 meV. Electron affinities of complex molecules are being determined with accuracies of approximately 0.2 eV through the use of a newly developed collisional ionization method [6–9].

The lowest negative ion state of a simple conjugated hydrocarbon results from the addition of an electron into a π-molecular orbital, and the energy of this vacant orbital is determined by the structure of the molecule. The large variety of conjugated hydrocarbons allows for considerable range in "π-electron affinities," and both bound and virtual states are known to exist.

It can be inferred from the theorem of Koopmans [10] that the Hartree-Fock energy of the lowest vacant molecular orbital, $\varepsilon_{\mathrm{LVMO}}$, gives an approximation to the electron affinity. Many attempts have been made to correlate measured electron affinity values with the molecular orbital energy $\varepsilon_{\mathrm{LVMO}}$. Becker and Chen [11], for example, found a definite linear correlation between the electron affinity values of Wentworth *et al.* [12] and the energy of the lowest vacant SCF-MO.

In the present work we have calculated energy levels for some conjugated systems using a semi-empirical, self-consistent field molecular orbital (SCF-MO) method. The method of Kunii and Kuroda [13] was used in order to compare directly with their earlier results. The unfilled molecular orbital energies are correlated with adiabatic electron affinities and negative ion resonance energies determined from recent beam experiments in order to predict energy states for other organic negative ions.

2. Theory

2.1. Hückel Method

Simple Hückel molecular orbital (HMO) calculations are made initially to obtain a first approximation to the molecular orbitals for use in the SCF-MO method. For conjugated hydrocarbons, the empirical values for the Coulomb integral, α_0, and the bond integral, β_0, are taken to be -6.24 eV and -3.14 eV, respectively, as determined by Wacks and Dibeler [14]. These values are modified for heteromolecules by using the relations

$$\alpha = \alpha_0 + h\beta_0, \tag{1}$$

$$\beta = k\beta_0. \tag{2}$$

The h and k are experimental quantities based on electronegativities and bond distances, respectively. The values used for these parameters are given in Table 1 for the core atoms under consideration.

2.2. Self-Consistent Field Method

Energy levels have been calculated for some conjugated systems containing C, N, and O atoms using a semi-empirical SCF-MO method based upon a variable β-γ modification of the Pariser-Parr-Pople approximation to the Hartree-Fock

Table 1. HMO parameters h and k

Core Atom	Index	h	Bond	k
C^+	1	0[a]	C–C	1.0[a]
N^+	2	1.5[b]	C=C	1.0[a]
N^{++}	3	1.5[b]	C–N	0.9[b]
O^+	4	2.0[b]	C≡N	0.9[b]
O^{++}	5	2.0[b]	C–O	0.34[b]
C^+(C≡N)	7	0[a]	C–S	0.68[c]
N^+(C≡N)	8	1.5[b]	C–Se	0.68[c]

[a] Ref.[42].

[b] Hess,B.A.Jr., Holyoke,C.W.Jr., Schaad,L.J.: Tetrahedron **28**, 3657 (1972).

[c] Hess,B.A.Jr., Schaad,L.J.: J. Am. Chem. Soc. **95**, 3907 (1973).

equation. The method of calculation is identical with that of Kunii and Kuroda [13] and others so that only a brief description will follow.

The so-called one-center electron repulsion integrals $\gamma_{\mu\mu}$ are approximated by

$$\gamma_{\mu\mu} = I_\mu - A_\mu \tag{3}$$

where A_μ is the valence state electron affinity of the μth core atom [15] and I_μ is the ionization potential of the charged core atom μ. The core energies, α_μ, are taken to be equal to I_μ. Values in eV for the parameters α_μ and $\gamma_{\mu\mu}$ are given in Table 2.

Table 2. SCF-MO parameters α_μ and $\gamma_{\mu\mu}$[a] (eV)

Core Atom	α_μ	$\gamma_{\mu\mu}$
C^+	−11.16	11.13
N^+	−14.12	12.34
N^{++}	−27.70	17.44
O^+	−17.70	15.23
O^{++}	−32.90	21.53
C^+(C≡N)	−12.69	10.09
N^+(C≡N)	−16.18	11.52

[a] Ohta,T., Kuroda,H., Kunii,T.L.: Theoret. Chim. Acta (Berl.) **19**, 167 (1970).

The two-center core integrals $\beta_{\mu\nu}$ and the two-center electron repulsion integrals $\gamma_{\mu\nu}$ are adjusted at each iteration until self-consistency is attained. The $\beta_{\mu\nu}$ terms are approximated by the prescription given by Nishimoto and Forster [16] for bonded atoms μ and ν by the relation

$$\beta_{\mu\nu} = A_0 + A_1 P_{\mu\nu}, \tag{4}$$

where the bond orders $P_{\mu\nu}$ are from the MO calculations of the previous iteration. The initial bond orders come from the HMO calculations. The empirical constants

Table 3. SCF-MO parameters A_0 and A_1 for integrals $\beta_{\mu\nu}$[a]

	A_0					A_1
Bond	$n^{b}=1$	2	3	4	$\geqslant 5$	all n
C–C	−2.04	−1.90	−1.84	−1.82	−1.81	−0.51
C–N	−2.24	−2.09	−2.02	−2.00	−1.98	−0.53
C–O	−2.44	−2.27	−2.20	−2.18	−2.17	−0.56
C≡N[c]	−2.24	−2.09	−2.02	−2.00	−1.98	−0.53

[a] Ref. [13]. [b] Number of benzene rings in molecules. [c] Estimated values for present work.

A_0 and A_1 are given in Table 3. The $\gamma_{\mu\nu}$ integrals are estimated for a pair of bonded atoms μ and ν by [17]

$$\gamma_{\mu\nu}=\frac{e^2}{a_{\mu\nu}+r_{\mu\nu}}, \tag{5}$$

where $a_{\mu\nu}$ is a constant of the bond and $r_{\mu\nu}$ is the bond distance. The constants $a_{\mu\nu}$ are derived from the reciprocal averages

$$\frac{1}{a_{\mu\nu}}=\frac{1}{2}\left(\frac{1}{a_{\mu\mu}}+\frac{1}{a_{\nu\nu}}\right), \tag{6}$$

where the constants $a_{\mu\mu}$ are taken to be inversely proportional to the one-center repulsion integrals $\gamma_{\mu\mu}$, such that

$$a_{\mu\mu}=\frac{e^2}{\gamma_{\mu\mu}}. \tag{7}$$

Combining Eqs. (6) and (7) gives

$$a_{\mu\nu}=\frac{2e^2}{\gamma_{\mu\mu}+\gamma_{\nu\nu}}. \tag{8}$$

Eliminating $a_{\mu\nu}$ from Eq. (5) results finally in

$$\gamma_{\mu\nu}=\frac{1}{(2/\gamma_{\mu\mu}+\gamma_{\nu\nu})+(r_{\mu\nu}/e^2)}. \tag{9}$$

The values for $\gamma_{\mu\nu}$ are adjusted at each iteration by varying the bond distances $r_{\mu\nu}$ according to the relation

$$r_{\mu\nu}=D_0+D_1P_{\mu\nu}. \tag{10}$$

The empirical constants D_0 and D_1 are taken from the work of Kunii and Kuroda [18] and given in Table 4.

The computer program was written in Fortran and runs on in IBM 360-91 computer. A list of the program can be obtained upon request.

Table 4. SCF-MO parameters D_0 and D_1 for bond distances $\gamma_{\mu\nu}$

Bond	D_0	D_1
C–C	1.517	−0.18
C–N	1.451	−0.18
C–O	1.410	−0.18
C=N[b]	1.309	−0.18

[a] Ref. [18].
[b] Estimated values for present work.

2.3. *Application of Koopmans' Theorem*

Within the approximation implicit in the use of Koopmans theorem [10], the electron affinity of a molecule is related to the energy of the lowest vacant molecular orbital, $\varepsilon_{\text{LVMO}}$, by

$$EA = -\varepsilon_{\text{LVMO}} - \delta. \tag{11}$$

δ is the "reorganization energy" correction and results from the fact that all of the electrons undergo relaxation upon addition of an extra electron. This relaxation can lead to considerable stabilization of the molecular ion [19]. A discussion of the influence of this "reorganization energy" on the stability of positive ions has been given by Heilbronner [20].

It is clear from the work of Cade [21] and others that Koopmans' theorem cannot be used to obtain satisfactory values for electron affinities of small molecules. The charge density of the electrons in the negative ion is not properly described by simply adding an electron to the lowest unfilled orbital of the molecule.

It is also known that the electron correlation is important in describing the stability of negative ions. In the cases when the neutral is a closed shell ground state system and the ion is open shell, simply taking the difference in the Hartree-Fock energies of the ion and neutral leads to an underestimate of the electron affinity. This may be reversed in cases where the neutral is an open shell species and the negative ion is a closed shell species. Thus, charge redistribution and electron correlation are two important factors influencing electron affinities which are neglected in applying Koopmans' theorem.

Nuclear relaxation in molecular negative ions can also provide considerable stabilization. This is particularly true for so-called "closed shell" molecules which undergo a gross change in geometry upon addition of an extra electron. Perhaps the most vivid example of this is the stability of the bent and extended CO_2^- ion as compared to its linear analogue [22].

In the present work we examine the applicability of Koopmans theorem as embodied in Eq. (11) for the estimation of electron affinities of some conjugated hydrocarbons. The severe restrictions imposed by the above mentioned inadequacies are partially accounted for in a semi-empirical calculation. As we shall see, an excellent linear relationship exists between $\varepsilon_{\text{LVMO}}$ and the measured values of the molecular electron affinities. This implies that the correction, δ, is approximately the same for all systems over a rather large range of electron binding energies. We should emphasize that the negative ion energy states calculated in this work pertain only to the addition of a "π-type" electron to the molecule. The calculations given here do not pertain to the cases when the additional electron is of "σ-type" or "n-type" (non-bonding lone pair).

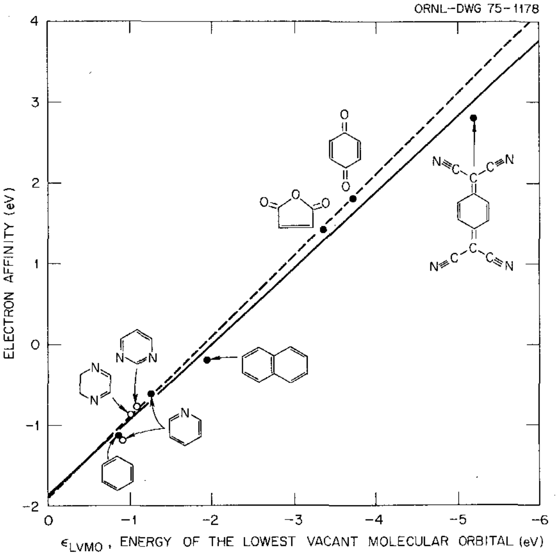

Fig. 1. Correlation of the energy of the lowest vacant molecular orbital, ε_{LVMO}, and electron affinities determined from beam experiments

3. Results and Discussion

The correlation of the lowest vacant orbital energy, ε_{LVMO}, and the electron affinities determined from the beam experiments of Schulz and of Compton are presented in Fig. 1. The molecules used in the correlation are given in Table 5

Table 5. Electron affinity and ε_{LVMO} values

Molecule	*EA* (eV)	ε_{LMVO} (eV)
Benzene	-1.14 ± 0.05^a	-0.87
Naphthalene	-0.20 ± 0.05^a	-1.94
Pyridine (1st res.)	-0.62 ± 0.05^a	-1.26
Pyridine (2nd res.)	-1.20 ± 0.05^a	-0.91
Pyrimidine (2nd res.)	-0.77 ± 0.05^a	-1.09
Pyrazine (2nd res.)	-0.87 ± 0.05^a	-1.01
Maleic Anhydride	1.4 ± 0.2^b	-3.35
Para-benzoquinone	1.8 ± 0.2^c	-3.71
TCNQ	2.8 ± 0.2^d	-5.12

[a] Ref. [5]. [b] Ref. [8]. [c] Ref. [9]. [d] Ref. [7].

along with measured electron affinities and molecular orbital energies. The solid data points represent the energies of the ground states of the negative ions while the open circles represent the first excited negative ion states. A least squares fit to the data gives the following equation:

$$EA = -0.95\varepsilon_{\mathrm{LVMO}} - 1.9 \text{ eV}. \tag{12}$$

The root mean square deviation from the mean for the intercept and the slope of this line was $\sigma = 0.09$ eV and $\sigma = 0.033$ eV, respectively. Although Koopmans' theorem predicts a slope of -1, we choose to use a least squares fit to the data for purposes of predicting other electron affinities. The dashed line in Fig. 1 is the previous correlation of Kunii and Kuroda [13] using electron affinities over the limited range from ~0.2 eV to 0.8 eV and is a line of unit slope with an intercept of -1.9 eV. The main difference in the two correlations results from the use of the data point for tetracyanoquinodimethan.

According to the SCF-MO calculations, the ground ${}^2E_{2u}$ state of the benzene negative ion is degenerate. This degeneracy is removed upon substitution of one, two, or three (asymmetrically placed) nitrogen atoms into the ring. The calculations show a splitting (~0.4 eV) of the pyridine negative ion state which is in good agreement with experiment [5, 23]. Nenner and Schulz [5] only reported a resonance for the first excited A^2A_u state for the pyrimidine and pyrazine negative ions. The ground ${}^2B$ states were suggested by these authors to be bound, and they estimated the electron affinities from polarographic potentials for the ground states of these two diazines and also *s*-triazine to be slightly positive. However, our calculations predict virtual states with electron affinities of -0.5 eV for pyrimidine, -0.3 eV for pyrazine, and -0.54 eV for *s*-triazine. At the present time we are experimentally searching for stable negative ions of these compounds in an attempt to resolve this apparent discrepancy.

Wentworth and Becker [24, 25] and Becker and Chen [11] have employed the electron capture method to determine the electron affinities of some aromatic hydrocarbons in the range from ~0.2 eV to ~0.8 eV. Table 6 contains a comparison of their electron affinity values with our predicted values. Except for azulene, the electron affinity values measured by Becker and Chen [11] are an average of 0.22 eV higher than our values. These are just within the estimated limits of error of our correlation. The values of Wentworth and Becker [24, 25] are in somewhat better agreement with ours. The close agreement in the case of the non-alternate hydrocarbon azulene is probably fortuitous, especially in view of the fact that azulene is believed to possess strain energy so that attachment of an electron requires a small "activation energy" (i.e., a change in molecular geometry occurs upon attachment of an electron [26]). Again, we emphasize that stabilization which might result from relaxation of the atomic nuclei in forming the ion is not taken into account in these calculations. A further example is the case of cycloöctatetraene, an alternant hydrocarbon which assumes a so-called "tub" form. Addition of an extra electron results in a planar anion. In view of this, our calculated electron affinity of 0.87 eV, which inherently assumes planarity in the carbon bonds, may be a reasonable estimate. Wentworth and Ristau [27] obtain an activation energy of 0.07 eV for electron attachment to cycloöctatetraene and an

Table 6. Comparison of electron affinity values

Molecule	ε_{LVMO} (eV)	EA (eV)	EA^a (eV)	EA^b (eV)
Naphthalene	−1.94	−0.06	0.148	
Anthracene	−2.52	0.49	0.556	0.42
Phenanthrene	−2.03	0.03	0.307	0.20
1,2-Benz-anthracene	−2.44	0.42	0.630	0.46
Chrysene	−2.27	0.26	0.397	0.33
3,4-Benz-phenanthrene	−2.19	0.18	0.545	0.33
Pyrene	−2.47	0.45	0.591	0.39
Triphenylene	−1.94	−0.06	0.285	0.14
4,5-Benz-pyrene	−2.37	0.35	0.534	
1,2-Benz-pyrene	−2.67	0.64	0.68	
1,2,5,6-Dibenz-anthracene	−2.39	0.37	0.595	
1,2,7,8-Dibenz-anthracene	−2.35	0.33	0.591	
Picene	−2.31	0.29	0.542	
Azulene	−2.81	0.77	0.656	

[a] Experimental electron affinities reported by Becker and Chen [11] using the common intercept method.

[b] Previous experimental electron affinities by Wentworth and Becker [12].

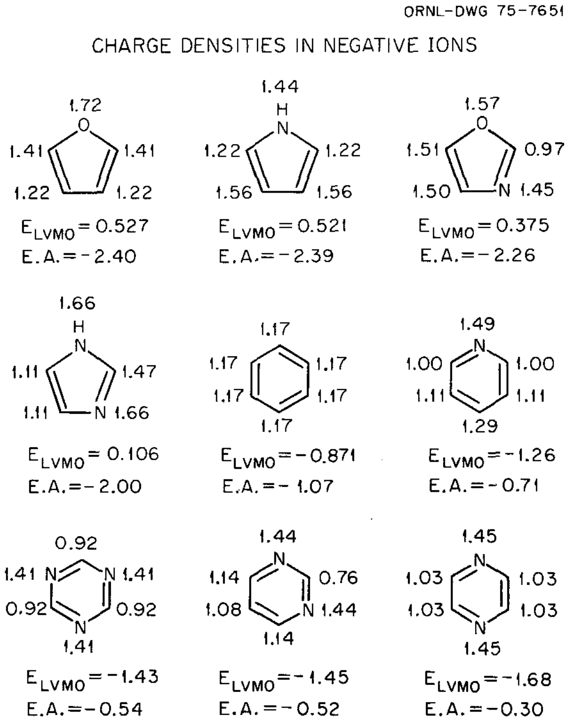

Fig. 2. The charge distributions were computed in terms of one electron wave functions. Net charge density at each atom in the negative ion is computed as the sum of twice the square of the charge distribution at each atom in each filled orbital of the neutral plus one times the square of the charge distribution at each atom in the first unfilled orbital of the neutral

electron affinity of 0.57 eV. Our calculations further predict a resonance at ~2.2 eV.

In order to better understand the molecular model being described, a study of conjugated systems which are iso-electronic to benzene was undertaken. Benzene, furan, imidazole, oxazole, pyrazine, pyrimidine, pyrrole, and *s*-triazine (all six π-electron systems) were examined and the charge densities corresponding to the negative ions were calculated. In Fig. 2 the molecules have been arranged in order of increasing electron affinities. Note that the five-member rings have smaller (more negative) electron affinities than the six-member rings. This can be explained qualitatively by the greater Coulomb repulsion between the π-electrons in the five-member rings. The progressions within the subset can be justified in terms of electronegativities and atomic orbitals. Charge distributions follow the expected electronegativity trends exactly. It is further expected that the electron affinity should increase with the number of heterocyclic substitutions. Except for *s*-triazine, this is the case. Due to high symmetry, the first and second unoccupied orbitals of *s*-triazine are degenerate and the energy splitting is suppressed in the calculation, which offers an explanation for the apparent anomaly. Oxygen is more electronegative than nitrogen, and thus atomic orbitals must be considered in order to understand why furan has a slightly smaller electron affinity than pyrrole and, similarly, why oxazole has a smaller electron affinity than imidazole. Furan and oxazole utilize the $2p_x$ and $2p_y$ atomic orbitals of oxygen to form σ-bonds with analogous carbon orbitals. The remaining $2p_z$ orbital contributes two electrons to the π-system. Pyrrole and imidazole both contain a nitrogen which is σ-bonded to two carbons and a hydrogen. These σ-bonds are formed from the $2p_x$, $2p_y$, and $2p_z$ atomic orbitals of nitrogen. In this configuration, nitrogen contributes two electrons to the π-system, but these electrons are from the $2s$ atomic orbital and hence are more tightly bound than the oxygen $2p_z$ π-electrons. Thus, Coulombic repulsion most probably accounts for the lower electron affinities of the oxygen heterocycles.

According to Matsen [28] the SCF-MO theory can be used to predict the work function of graphite. It is suggested that the ionization potential and electron affinity plotted as a function of the lowest allowed energy, $h\nu$, should be symmetrical about the work function of graphite [29]. Also, Hush and Pople [30] suggest that the sum of the ionization potential and electron affinity should be a constant for conjugated hydrocarbons. A determination of a reasonable number for the work function of graphite might be a good indicator of the accuracy of the present work.

With this objective in mind, a correlation of the highest occupied orbital energy, $\varepsilon_{\mathrm{HOMO}}$, and ionization potentials was made for some of the conjugated molecules used in the electron affinity correlation. Values of the ionization potential were taken from the work of Dewar and Worley [31] and Kotov and Potapov [32]. Pertinent data are given in Table 7. In Fig. 3 we plot the measured ionization potential versus the energy of the highest occupied molecular orbital ($\varepsilon_{\mathrm{HOMO}}$). The following equation results from a least squares fit to the data:

$$IP = -0.97\varepsilon_{\mathrm{HOMO}} - 0.68 \text{ eV}. \tag{13}$$

Table 7. Ionization potential and $\varepsilon_{\mathrm{HOMO}}$ values

Molecule	*IP* (eV)	$\varepsilon_{\mathrm{HOMO}}$ (eV)
Benzene	9.25[a]	−10.32
Naphthalene	8.12[a]	− 9.25
Pyridine	9.27[b]	−10.36
Pyrimidine	9.64[b]	−10.76
Pyrazine	9.29[b]	−10.39
Para-benzoquinone	9.96[a]	−10.97
TCNQ	9.42[a]	−10.01

[a] Ref. [32]. [b] Ref. [31].

Electron affinities and ionization potentials have been calculated for 28 hydrocarbons along with the energy of the lowest allowed transition energy ($\varepsilon_{\mathrm{LVMO}} - \varepsilon_{\mathrm{HOMO}}$). As expected, the two sets of data presented in Fig. 4 fall on two straight lines whose equations are

$$EA = -0.48h\nu + 3.43 \text{ eV} \tag{14}$$

and

$$IP = +0.48h\nu + 4.75 \text{ eV}. \tag{15}$$

The slopes of these two lines are very close to that expected from theory, i.e., −0.5 and +0.5, respectively [11]. The small difference is due, of course, to the

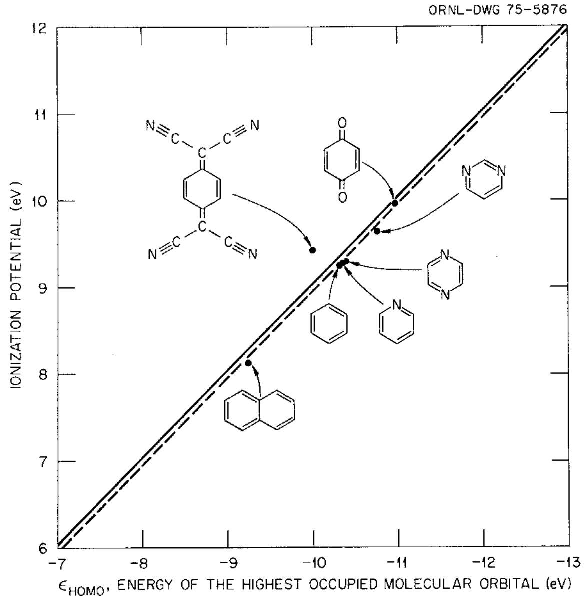

Fig. 3. Correlation of the energy of the highest occupied molecular orbital, $\varepsilon_{\mathrm{HOMO}}$, and experimentally determined ionization potentials

fact that the slopes of our correlation lines [Eqs. (12) and (13)] are $|0.96|$ rather than unity.

The sum of the electron affinity and ionization potential is indeed a constant equal to 8.18 eV as compared to a value of 8.34 eV determined by Becker and Chen [11] and 8.24 eV reported by Wentworth and Becker [12]. The point at which $h\nu \rightarrow 0$ should represent graphite. The zero intercepts in Fig. 3 yield an electron affinity and ionization potential of graphite of 3.43 eV and 4.75 eV, respectively. These values agree rather well with the values reported by Becker and Chen [11] of 3.02 eV and 4.71 eV, respectively. Now the molecular electronegativity is defined by

$$\chi = \tfrac{1}{2}(EA + IP) \tag{16}$$

and has a value of 4.09 eV for the conjugated hydrocarbons reported in Table 8. Thus, the ionization potential and electron affinity are symmetrical about χ. Matsen [28] and Hush and Pople [30] have taken the molecular electronegativity to be the work function of graphite. They further observe that the ionization potential equals the electron affinity at this point. This result was predicted based upon Koopmans' theorem without consideration of the reorganization energies. The difference in our reorganization energy is 1.22 eV and qualitatively explains

Table 8. Electron affinities, ionization potentials, and lowest energies

Molecule	$\varepsilon_{\mathrm{LVMO}}$ (eV)	EA (eV)	$\varepsilon_{\mathrm{HOMO}}$	IP (eV)	$\varepsilon_{\mathrm{LVMO}} - \varepsilon_{\mathrm{HOMO}}$ (eV)
Benzene	−0.87	−1.07	−10.32	9.33	9.45
Naphthalene	−1.94	−0.06	− 9.25	8.29	7.31
Phenanthrene	−2.03	−0.03	− 9.16	8.21	7.13
Anthracene	−2.52	0.49	− 8.67	7.73	6.15
Triphenylene	−1.94	−0.06	− 9.25	8.29	7.31
3,4-Benz-phenanthrene	−2.19	0.18	− 9.00	8.05	6.81
Chrysene	−2.27	0.26	− 8.92	7.97	6.65
1,2-Benz-anthracene	−2.44	0.42	− 8.75	7.81	6.31
Pyrene	−2.47	0.45	− 8.72	7.78	6.25
Naphthacene	−2.88	0.84	− 8.31	7.38	5.43
3,4,5,6-Dibenz-phenanthrene	−2.27	0.26	− 8.92	7.97	6.65
Picene	−2.31	0.29	− 8.88	7.93	6.57
1,2,7,8-Dibenz-anthracene	−2.35	0.33	− 8.84	7.89	6.49
1,2,3,4-Dibenz-anthracene	−2.36	0.34	− 8.83	7.89	6.47
1,2,5,6-Dibenz-anthracene	−2.39	0.37	− 8.80	7.86	6.41
Pentaphene	−2.46	0.44	− 8.73	7.79	6.27
4,5-Benz-pyrene	−2.37	0.35	− 8.82	7.88	6.45
1,2-Benz-pyrene	−2.67	0.64	− 8.52	7.58	5.85
Perylene	−2.75	0.71	− 8.44	7.51	5.69
Pentacene	−3.12	1.06	− 8.07	7.15	4.95
Hexahelicene	−2.27	0.26	− 8.92	7.97	6.65
1,12-Benz-perylene	−2.54	0.51	− 8.65	7.71	6.11
Coronene	−2.34	0.32	− 8.85	7.90	6.51
Ovalene	−2.85	0.81	− 8.34	7.41	5.49
Hexacene	−3.29	1.23	− 7.90	6.98	4.61
Heptacene	−3.41	1.34	− 7.78	6.87	4.37
Octacene	−3.50	1.43	− 7.69	6.78	4.19
Novacene	−3.57	1.49	− 7.62	6.71	4.05

the difference in ionization potential and electron affinity of 1.32 eV for graphite as derived from Fig. 4.

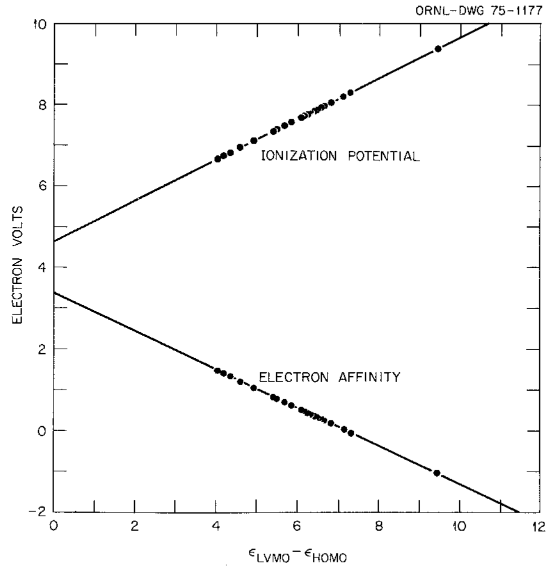

Fig. 4. Correlations of electron affinity and ionization potential with lowest electronic transition energy, $\varepsilon_{\mathrm{LVMO}}-\varepsilon_{\mathrm{HOMO}}$

The graphite under consideration is an infinite two-dimensional molecule (graphite sheet) and has been referred to as "gaseous graphite." By plotting the electron affinities and ionization potentials as a function of the number of benzene rings in a hydrocarbon molecule, the values for graphite should be approached as the number of rings increases to infinity, though such an extrapolation to a large number of rings is impracticable in two dimensions. However, a one-dimensional approximation for graphite can be obtained by considering only the linear chain of benzene rings. Values of the electron affinity, ionization potential, and number of benzene rings are given in Table 9 and plotted in Fig. 5. Various mathematical

Table 9. Electron affinity, ionization potential, and number of linear rings

Molecule	*EA*	*IP*	*N*
Benzene	−1.07	9.33	1
Naphthalene	−0.06	8.29	2
Anthracene	0.49	7.73	3
Naphthacene	0.84	7.38	4
Pentacene	1.06	7.15	5
Hexacene	1.23	6.98	6
Heptacene	1.34	6.87	7
Octacene	1.43	6.78	8
Novacene	1.49	6.71	9

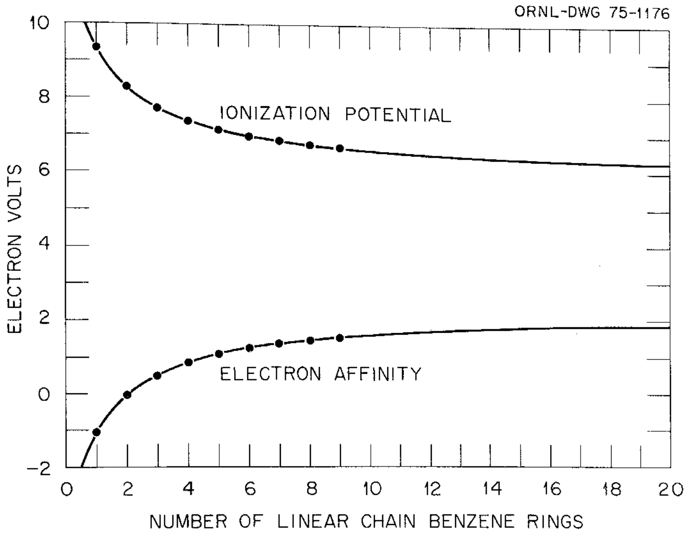

Fig. 5. Electron affinity and ionization potential versus the number of linear chain benzene rings

forms were considered in extrapolating the data; however, the best fit seemed to be a hyperbola (solid lines in Fig. 4) which are asymptotic to values of 2.21 eV for the electron affinity and 5.99 eV for the ionization potential. These values agree rather well with the results obtained by Becker and Chen [11] for the ^1L_a transition of 2.23 eV and 5.6 eV, respectively. The electronegativity value of 4.1 eV obtained from these data agrees well with that of Wentworth and Becker [12] of 4.07 eV and Becker and Chen [11] of 4.17 eV.

Thirty years ago Mulliken [33] and Braun and Busch [34] reported an experimental value for the work function of graphite to be 4.39 eV. However, a more recent determination by Willis *et al.* [35] indicates a value of 4.7 eV. Our calculations pertain to graphite vapor, and thus a direct comparison with experiment is not entirely justified. In any event, the exact work function (±0.1 eV) is uncertain. Since the work function of graphite is a statistical quantity, in that an electron is removed from the top of the Fermi level [36], it appears that the value should be in the range from about 3.5 eV to 4.7 eV and most probably should occur near 4.1 eV for graphite vapor.

The semi-empirical calculations presented here appear to account adequately for electron affinities of all conjugated hydrocarbons where reliable measurements exist. It is interesting to consider the applicability of the present theory to excited negative ion states. Nenner and Schulz [5] have presented data on the energy positions of the $\tilde{A}^2B_{2g}$, $\tilde{B}^2B_1$, and $\tilde{B}^2B_{2g}$ negative ion states of benzene, pyridine, and pyrazine, respectively. The lifetimes of these compound states are sufficiently short so that vibrational progressions were not observed and the resonances were rather broad (~1.5 eV). Using Eq. (12), we calculate the resonance energies to be 3.97 eV, 3.83 eV, and 3.67 eV for benzene, pyridine, and pyrazine, respectively. These values agree with the onsets for the states reported by Nenner and

Table 10. Calculated electron affinities and excited state negative ion energy levels for some conjugated organic molecules. The lowest vacant and the second and third lowest vacant orbitals are included

Molecule	ε_{LVMO} (eV)	*EA* (eV)	ε_{2VMO} (eV)	1st Excited State (eV)	ε_{3VMO} (eV)	2nd Excited State (eV)
Acenaphthylene	−2.81	0.77	−1.25	−0.71	−0.15	−1.76
Acridine	−2.79	0.75	−1.36	−0.61	−1.06	−0.89
Acrylonitrile	−3.38	1.31	−0.47	−1.45	—	—
Adenine	−1.75	−0.24	−1.26	−0.70	0.06	−1.96
Alloxan	−3.50	1.43	−0.59	−1.34	−0.55	−1.38
Aniline	−1.39	−0.58	−1.26	−0.70	1.52	−3.34
Anthracene	−2.52	0.49	−1.32	−0.65	−1.03	−0.92
Azulene	−2.81	0.77	−1.94	−0.06	0.72	−2.58
Benzene	−0.87^{a}	−1.07	2.18	−3.97	—	—
Para-benzoquinone	−3.71	1.62	−1.08	−0.87	−0.13	−1.78
1,2-Benz-anthracene	−2.44	0.42	−1.83	−0.16	−1.22	−0.74
1,12-Benz-perylene	−2.54	0.51	−1.97	−0.03	−1.17	−0.79
3,4-Benz-phenanthrene	−2.19	0.18	−1.94	−0.06	−1.11	−0.85
1,2-Benz-pyrene	−2.67	0.64	−1.74	−0.25	−1.22	−0.74
4,5-Benz-pyrene	−2.37	0.35	−1.89	−0.10	−1.21	−0.75
1,2,3,4-Dibenz-anthracene	−2.36	0.34	−1.90	−0.10	−1.64	−0.34
1,2,5,6-Dibenz-anthracene	−2.39	0.37	−1.98	−0.02	−1.58	−0.40
1,2,7,8-Dibenz-anthracene	−2.35	0.33	−2.07	0.07	−1.38	−0.59
3,4,5,6-Dibenz-phenanthrene	−2.27	0.26	−2.02	0.02	−1.58	−0.40
Biphenyl	−1.78	−0.21	−1.00^{a}	−0.95	−0.27	−1.64
Biphenylene	−1.65	−0.33	−1.27	−0.69	−0.83	−1.11
1,3-Butadiene	−1.46	−0.51	1.07	−2.92	—	—
Carbazole	−1.63	−0.35	−1.24	−0.72	−0.40	−1.52
Chrysene	−2.27	0.26	−1.75	−0.24	−1.38	−0.59
Coronene	−2.34^{a}	0.32	−1.18^{a}	−0.78	−0.92	−1.03
Cytosine	−1.97	−0.03	−0.84	−1.10	1.40	−3.23
Ethylene	−0.31	−1.61	—	—	—	—
Fluoranthene	−2.66	0.63	−1.30	−0.67	−1.25	−0.71
Fulvalene	−3.82	1.73	−0.41	−1.51	0.79^{a}	−2.65
Fumaronitrile	−4.38	2.26	−2.38	0.36	0.07	−1.97
Furan	0.53	−2.40	0.80	−2.66	—	—
Glyoxal	−2.99	0.94	0.07	−1.97	—	—
Guanine	−1.10	−0.86	−0.54	−1.39	0.35	−2.23
Heptacene	−3.41	1.34	−2.62	0.59	−1.81	−0.18
Heptafulvalene	−2.19^{a}	0.18	−1.93	−0.07	0.55	−2.42
Hexacene	−3.29	1.23	−2.37	0.35	−1.47	−0.50
Hexahelicene	−2.27	0.26	−2.20	0.19	−1.61	−0.37
Imidazole	0.11	−2.00	0.67	−2.54	—	—
Isoquinoline	−2.07	0.07	−1.34	−0.63	−0.30	−1.62
Maleic Anhydride	−3.35	1.28	0.73	−2.59	0.94	−2.79
Maleimide	−3.21	1.15	0.73	−2.59	0.81	−2.67
Naphthacene	−2.88	0.84	−1.62	−0.36	−1.39	−0.58
Naphthalene	−1.94	−0.06	−1.18	−0.78	−0.22	−1.69
1,5-Naphthyridine	−2.45	0.43	−1.24	−0.72	−0.57	−1.36
1,6-Naphthyridine	−2.31	0.29	−1.35	−0.62	−0.46	−1.46
1,7-Naphthyridine	−2.36	0.34	−1.38	−0.59	−0.46	−1.46
1,8-Naphthyridine	−2.43	0.41	−1.23	−0.73	−0.51	−1.42
2,6-Naphthyridine	−2.27	0.26	−1.45	−0.52	−0.41	−1.51
2,7-Naphthyridine	−2.15	0.14	−1.53	−0.45	−0.36	−1.56
Novacene	−3.57	1.49	−2.96	0.91	−2.31	0.29
Octacene	−3.50	1.43	−2.81	0.77	−2.08	0.08

Table 10 (continued)

Molecule	ε_{LVMO} (eV)	*EA* (eV)	ε_{2VMO} (eV)	1st Excited State (eV)	ε_{3VMO} (eV)	2nd Excited State (eV)
Ovalene	−2.85	0.81	−2.23	0.22	−1.72	−0.27
Oxazole	0.37	−2.25	0.54	−2.41	—	—
Parabanic Acid	−2.95	0.90	0.50	−2.38	0.87	−2.73
Para-Phenylenediamine	−1.75	−0.24	−1.55	−0.43	0.98	−2.83
Pentacene	−3.12	1.06	−2.05	0.05	−1.42	−0.55
Pentaphene	−2.46	0.44	−2.29	0.28	−1.34	−0.63
Perylene	−2.75	0.71	−1.25[a]	−0.71	−1.18	−0.78
Phenanthrene	−2.03	0.03	−1.72	−0.27	−0.82	−1.12
Phenazine	−3.12	1.06	−1.40	−0.57	−1.14	−0.82
Phenol	−1.31	−0.66	−1.12	−0.84	1.64	−3.46
Picene	−2.31	0.29	−1.99	−0.01	−1.54	−0.44
Purine	−1.92	−0.08	−0.93	−1.02	0.51	−2.38
Pyrazine	−1.68	−0.30	−1.01	−0.94	1.87	−3.68
Pyrene	−2.47	0.45	−1.60	−0.38	−1.01	−0.94
Pyridine	−1.26	−0.70	−0.91	−1.04	2.03	−3.83
Pyrimidine	−1.45	−0.52	−1.09	−0.86	1.89	−3.70
Pyrrole	0.52	−2.39	0.70	−2.57	—	—
Quinazoline	−2.32	0.30	−1.33	−0.64	−0.43	−1.49
Quinoline	−2.21	0.20	−1.21	−0.75	−0.37	−1.55
Quinoxaline	−2.54	0.51	−1.27	−0.69	−0.50	−1.43
Styrene	−1.59	−0.39	−0.85	−1.09	0.39	−2.27
TCNE (tetracyanoethylene)	−5.21	3.05	−3.20[a]	1.14	−1.90	−0.10
TCNQ (tetracyanoquinodimethan)	−5.12	2.96	−2.92[a]	0.87	−2.48	0.46
TNAP (tetracyanonaphthalene)	−5.11	2.95	−2.96	0.91	−2.80	0.76
s-Triazine	−1.43[a]	−0.54	1.75	−3.56	—	—
Triphenylene	−1.94[a]	−0.06	−1.37	−0.60	−0.45[a]	−1.47
Uracil	−1.86	−0.13	−0.23	−1.68	2.01	−3.81
Vinylene Carbonate	−0.32	−1.60	1.55	−3.37	—	—
Vinylidene Cyanide	−3.74	1.65	−2.94	0.89	0.23	−2.12

[a] Designates degenerate orbital.

Schulz [5] to within 0.2 eV. In each of these cases the onset was difficult to ascertain because of the breadth of the resonance. The theory, however, does seem to predict the approximate positions of the resonances surprisingly well. The present theory has also been used to adequately predict compound states observed in para-benzoquinone [9] and TCNQ [7]. The ability of the present theory to predict the position of the excited negative ion states implies that the so-called "reorganization energy" is approximately the same in the excited state as in the ground state.

In Table 10 we present calculations of the adiabatic electron affinities and the energies of the first two excited negative ion states (note degeneracies) for a number of conjugated hydrocarbons and heteromolecules of physical and biological interest. The electron affinity values seem to be consistent with what is known about the stability of these negative ions. In the following we briefly itemize a few comments about the computed electron affinities in Table 10 and experimental values.

(1) In all cases where a stable negative ion is known to exist, a positive electron

affinity is calculated. For example, heptafulvalene is predicted to have a positive electron affinity. We have, in fact, observed thermal electron attachment to heptafulvalene molecules in the gas phase (unpublished).

(2) A compound state has been observed previously as a broad and structureless dip at an energy of 1.7 eV in the electron transmission spectra of ethylene (see Ref. [37]). Burrow and Jordan [38] have recently observed vibrational structure in this resonance and obtain an electron affinity of -1.55 ± 0.1 eV for ethylene. We calculated that the ${}^2B_{2g}$ state of $C_2H_4^-$ should occur at 1.61 eV.

(3) Burrow and Jordan [38] have also measured an electron affinity of -0.62 ± 0.05 eV for 1,3-butadiene which is in excellent agreement with our calculated value of -0.51 eV. Further, Burrow and Jordan [38] assign a feature in the total scattering cross section for electrons in 1,3-butadiene at 2.8 ± 0.1 eV as due to attachment of an electron into the second unfilled π^* orbital ($2b_g$). We calculate the first excited negative ion state of 1,3-butadiene to be at 2.9 eV.

(4) Chen and Wentworth [39] have recently made a comparison of experimental determinations of electron affinities of π-charge transfer complex acceptors and arrive at the following electron affinities which can be compared with those in Table 10: TCNE (2.77–2.9 eV); TCNQ (2.84–2.88 eV); maleic anhydride (1.33–1.65 eV); *p*-benzoquinone (1.83–1.98 eV). All of these values are in excellent agreement with the values reported in Table 10.

The only major contradiction to the theoretical predictions to electron affinities in this work is the report of Christophorou *et al.* [40] that the electron affinity of benzene is positive. These authors argue that relaxation of the nuclei may allow for a positive electron affinity; however, Nenner and Schulz [5] present evidence that this is not the case and, in fact, suggest that little deformation occurs in going from the neutral to the ion.

It is interesting to note that all of the molecules possessing the $=C(CN)_2$ groups are predicted to have at least one and perhaps two bound excited states. Our result that the electron affinities of TCNQ (tetracyanoquinodimethan), TCNE (tetracyanoethylene), and TNAP (tetracyanoquinonaphthalene) are all approximately identical appears, upon first sight, suspicious. Experimental measurements of the electron affinities on the latter two compounds are presently underway in our laboratory. The experimental value for TCNE determined by Faragher and Page [41] of 2.88 eV is in agreement with the value reported in this work; however, Lyons and Palmer [42], using essentially the same technique, report a value of 1.7 ± 0.3 eV. The lower value for the electron affinity is supported somewhat by the photodetachment threshold of Lyons and Palmer [43] for TCNE of 2.03 ± 0.07 eV. However, Chen and Wentworth [39] present evidence for a value of 2.8 eV.

Fluoranthene is an interesting molecule in which to consider the attachment of an electron and to consider the energy levels of the negative ion. Fluoranthene is one of the stable exceptions to Hückel's $4n+2$ rule [44] and is sometimes viewed as two separate π-systems (benzene and naphthalene) connected by sigma bonds. We previously observed [45] at least two compound negative ion states in fluoranthene. One resonance was long-lived and peaked at 0.2 eV and another short-lived state occurred at ~2.6 eV. The position at each resonance was explained in

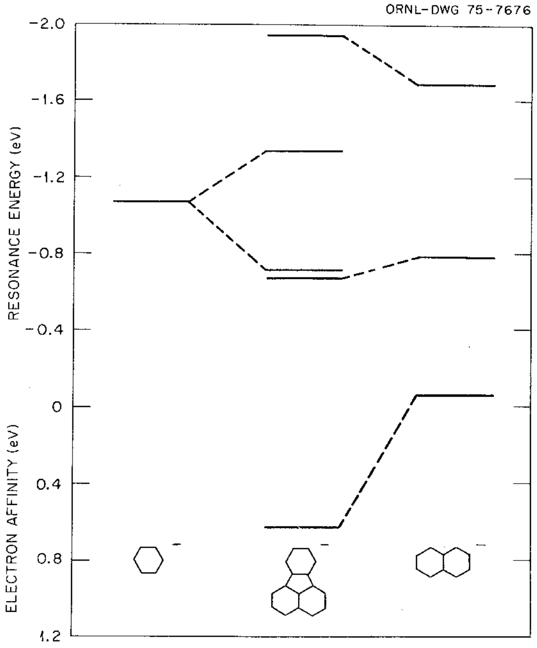

Fig. 6. Electron affinities were calculated for benzene, fluoranthene, and naphthalene. Each of the fluoranthene lowest vacant molecular orbitals was paired with the molecular orbital of benzene or naphthalene which appeared to dominate it in terms of charge distribution, symmetry, and energy

terms of perturbative coupling of benzene and naphthalene, each of which exhibits a resonance. The perturbative term in the Hamiltonian was calculated to be ~0.9 eV [45]. In the present work we have examined the charge distributions for each unoccupied orbital and paired each fluoranthene orbital with the submolecular orbital which it most closely resembles in terms of charge distribution, symmetry, and energy. Fig. 6 shows the calculated energy levels along with the pairings of the levels for each molecule. From this analysis we obtain a perturbation of ~0.7 eV, in reasonable agreement with that obtained earlier [45].

Azulene also deserves special mention in that a number of experimental facts are known about its negative ion properties. The electron affinity of azulene has been measured to be 0.66 eV (see Table 6). A resonance in the attachment rate found at ~0.22 eV to 0.37 eV was reported by Chaney *et al.* [46]. Also, a resonance peaking at 2.44 eV (vibrational structure of ~0.17 eV) has been observed in azulene using the SF_6^- scavenger technique [47]. In the present work (see Table 10) we calculate an electron affinity of 0.77 eV, with resonances at 0.06 eV and 2.58 eV, which agrees reasonably well with the experimental facts. We suggest that the data contained in Table 10 will be helpful in interpreting negative ion energy levels in other organic systems.

Finally, we consider the additivity of group substitutions to electron affinities. Faragher and Page [41, 48] have analyzed electron affinity data for a number of molecules containing the cyano group and have suggested that a –CN group

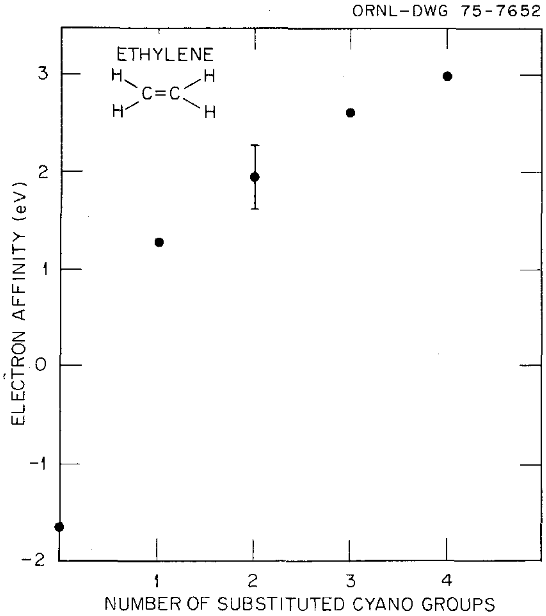

Fig. 7. Electron affinities for ethylene with varying numbers of –CN groups substituted for hydrogen were calculated. When more than one isomer was possible, the average electron affinity was plotted with the spread in values indicated by "error bars"

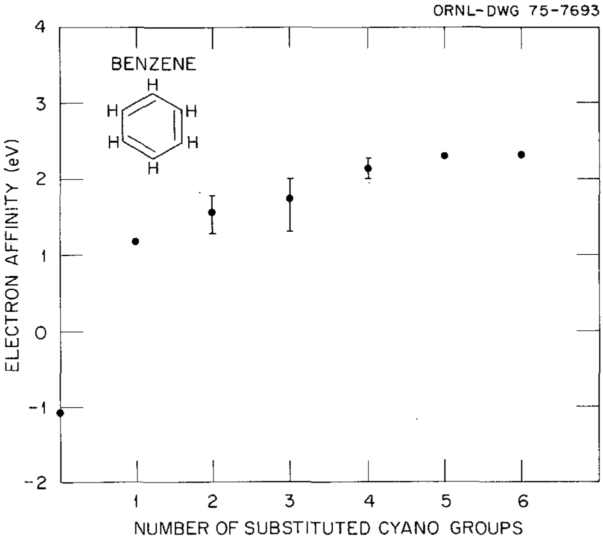

Fig. 8. Electron affinities for benzene with varying numbers of –CN groups substituted for hydrogen were calculated. When more than one isomer was possible, the average electron affinity was plotted with the spread in values indicated by "error bars"

contributes ~0.55 eV to the electron affinity of a conjugated hydrocarbon. A study of electron affinities for ethylene, benzene, and naphthalene with varying numbers of –CN groups substituted for hydrogens was conducted in which all combinations were considered. Figs. 7 and 8 show the calculated variation of electron affinity versus number of substituted –CN groups for ethylene and benzene. When more than one isomer was possible, the average electron affinity was plotted with the spread in values indicated by "error bars." The apparent saturation effect observed is physically understandable in that the amount of perturbation caused by the first substitution would be greater than the amount caused by the second, etc. Our calculated electron affinities for sym-tetracyanobenzene and hexacyanobenzene are in excellent agreement with the experimental values determined by Faragher and Page [41] who used the magnetron method. Our estimated value of ~1.1 eV for benzonitrile is considerably higher than the recent value of 0.24 eV reported by Wentworth *et al.* [49].

In conclusion, we feel that the simple molecular orbital method employed by Kunii and Kuroda [13] and here is highly useful in predicting adiabatic electron affinities and compound negative ion states in complex molecules. The theory appears adequate to account for most of the experimental facts which are known about conjugated molecular negative ion systems.

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