MNDO Studies on Electron Affinity and Ionization Potentials of Polycyano Derivatives of some Unsaturated Hydrocarbons and Benzene

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Semiempirical MNDO calculations with optimization of geometry were carried out for several polycyano derivatives of some unsaturated hydrocarbons and benzene. The results show that the MNDO method overestimates the AEA's (adiabatic electron affinity) by about 0.575 eV, as is seen from the equation $\mathrm{AEA}_{\mathrm{exp}} = 0.998\ \mathrm{AEA}_{\mathrm{MNDO}} - 0.575$; $R = 0.9995$. It was found that there exists a linear correlation between the energies of LUMO and the AEA's of the investigated compounds: $\mathrm{AEA} = -\ 1078\ \mathrm{LUMO} + 0.387$; $R = 0.9979$ for 40 points.

MNDO does not show a linear correlation of AEA with IP (ionization potential). Generally, with increasing number of cyano substituents in unsaturated hydrocarbons the energy of HOMO and LUMO decreases, but this may not necessarily be true for higher molecular orbitals.

Introduction

The adiabatic electron affinity is defined as the difference of the heat of formation of a neutral molecule (in its lowest rotational-vibrational state) and the heat of formation of its anion (in its lowest rotational-vibrational state) after addition of one electron: $\mathrm{AEA} = \Delta H^0 - \Delta H^-$. It is well known that AEA may carry information on (i) the thermochemistry of the reaction of ions with neutral molecules in the gas phase [1] which is essential when the stability of charge transfer complexes (CT) is investigated and (ii) the reactivity models involving CT complexes in the cyclisation reactions [2]. Further (iii) the AEA and the ionisation potential, IP, are the reactivity indexes of the molecule in the reaction with nucleophiles and electrophiles, respectively [3], and (iv) changes in AEA and IP of the molecule reflect the electronic effects of the substituents on the reactivity of the molecule, and therefore are immediately related to the energy shape of the frontier orbitals, HOMO and LUMO.

Within the approximation implicit in the use of Koopman's theorem, the electron affinity of a molecule is related to the energy of the vacant molecular orbital LUMO, by $\mathrm{AEA} = E_{\mathrm{LUMO}} - \delta$, where δ is the "reorganization" correction and results from the fact that all electrons undergo relaxation upon addition of an extra electron [4].

Because of the experimental difficulties more precise measurements of AEA were made after 1968 [5], and only in the last decade there were developed new techniques such as mass spectrometry of negative ions [6] and magnetronic measurements [7] which allowed to evaluate AEA's of molecules with reliable accuracy.

Ab initio calculations of AEA for small molecules were made and gave reasonable results [8]. The calculations consume, however, so much computational time that they cannot be used for larger molecules yet. The semiempirical methods are suitable for calculations of AEA if the geometry is optimized for the neutral molecule and its anion formed by the addition of an electron.

We have chosen the MNDO method of Dewar and Rzepa [9] to calculate AEA's of polycyano derivatives of ethylene, benzene, fulvene, dimethylenecyclobutane, methylenecyclopropane, trimethylene cyclopropane, dimethylenequinone, butadiene and methylenecycloheptatriene.

We were interested in the following questions: (i) what is the accuracy of the MNDO evaluated AEA's of polycyano derivatives of some unsaturated hydrocarbons when compared with the known experimental data, (ii) what is the k value in the correlation equation $\mathrm{AEA} = k\,E_{\mathrm{LUMO}} - \delta$ and is δ constant for all of the investigated series? (iii) does the AEA correlate linearly with the number of the

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cyano substituents within the serie? (iv) does there exist a linear correlation of AEA with IP, as it might be expected from Houk and Munchausen [2d] suggestion?

Calculations

Dewar and Thiel's version of the MNDO procedure (Modified Neglect of Diatomic Overlap), adopted for a CDC 6600 computer, was used [10]. The molecular geometry of the neutral molecules was calculated by minimizing the total energy with respect to all geometrical variables, using the Davidon-Fletcher-Powell method [11], within the symmetry of the molecules given in Table 2, and within the close-shell approximation. The geometry of the anions was optimized using the half-electron (h-e) approximation for the open shell system, starting with the geometry of the neutral molecule [12].

Results and Discussion

Accuracy of the MNDO method in evaluation of AEA's

The accuracy of the MNDO method in calculations of the AEA of some polycyano derivatives of unsaturated hydrocarbons, for which experimental data are known, can be seen in Table 2. We were looking for a correlation between AEA_{exp} and AEA_{calc} and found the linear relation $AEA_{exp} = 0.998\,AEA_{MNDO} - 0.575$ ($R = 0.9995$, standard deviation 0.02 eV), for the first 7 compounds of Table 1. The MNDO method seems to overestimate the AEA by 0.58 eV since the slope of the correlation equation is very close to unity (Figure 1). The AEA's of the last 3 compounds in Table 1 deviate considerably from the correlation and were not included into the correlation. The ground states of the neutral molecules of benzene and hexacyanobenzene are of D_{6h} symmetry, so the ground states of their anions are doubly degenerated by the Jahn-Teller effect. MNDO overestimates the AEA of these two compounds by 1.05 and 0.8 eV respectively, that is by about 0.5 and 0.2 eV more than is foreseen by the applied correlation equation. It seems that the energy changes of these two compounds connected with the Jahn-Teller effect are not very well reproduced by MNDO, none the less the calculations for anions were performed in the C_{2v} point group and the observed geometry changes connected with this effect are small. However, there is no good explanation for the deviation of AEA_{MNDO} of benzene and hexacyanobenzene from the applied correlation yet.

As it is seen from Fig. 1 and the correlation equation, two experimental values of TCNE, 2.88 and 2.03 eV seem to be incorrect and therefore were

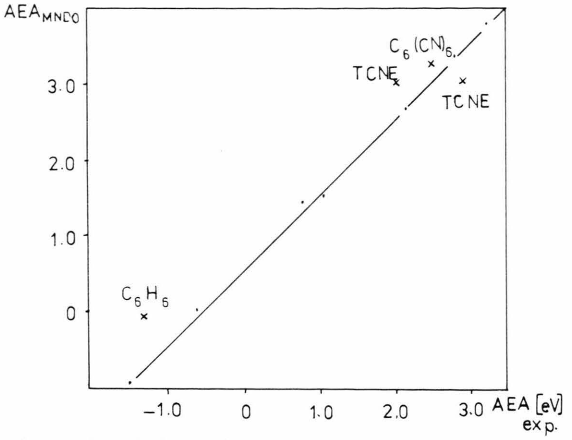


Fig. 1. Correlation of AEA_{exp} with AEA_{MNDO} of the compounds given in Table 1.

Table 1. The calculated and experimental adiabatic electron affinity, AEA, of some polycyano derivatives.

Compound	AEA_{MNDO} [eV]	AEA_{exp} [eV]
1,2-Dicyanobenzene	1.55	1.04 ± 0.1 [2]
1,2,4,5-Tetracyanobenzene	2.71	2.15 ± 0.22 [2]
Ethylene	−1.02 [1]	−1.55 [3]
trans-1,2-Dicyanoethylene	1.44	0.78 ± 0.1 [4]
Bis(dicyanomethylene)-p-quinone	3.42 [1]	2.80 ± 0.17 [5]
trans 1,3-Butadiene	0.0 [1]	−0.62 [3]
Hexacyanobutadiene	3.79	3.24 ± 0.05 [6]
Benzene	−0.09 −0.07 [1]	−1.14 ± 0.05 [6]
Hexacyanobenzene	3.27	2.48 ± 0.13 [2]
Tetracyanoethylene	3.06 [1]	2.88 [2] 2.03 [7]

[1] M. S. J. Dewar and H. S. Rzepa, J. Amer. Chem. Soc. **100,** 784 (1978).

[2] E. C. Chen and W. E. Wentworth, J. Chem. Phys. **63,** 3183 (1975); **65,** 237 (1977).

[3] P. D. Burrow and K. D. Jordan, Chem. Phys. Lett. **36,** 594 (1975).

[4] A. L. Farrangher and F. M. Page, Trans. Farad. Soc. **63,** 2369 (1967).

[5] C. E. Klots, R. N. Compton, and V. F. Raaen, J. Chem. Phys. **60,** 1177 (1975).

[6] I. Nenner and J. G. Schulz, J. Chem. Phys. **62,** 1147 (1975); K. D. Jordan, J. A. Michejda, and P. D. Burrow, J. Amer. Chem. Soc. 1295, 7189 (1976).

[7] L. E. Lyons and L. D. Palmer, Chem. Phys. Lett. **21,** 442 (1973).

Table 2. The calculated adiabatic electron affinity, ionization potential and energy of LUMO orbitals of some unsaturated hydrocarbons and benzene.

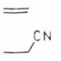
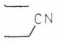
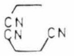
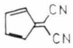
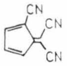
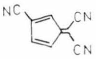
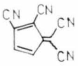
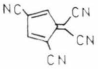
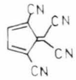
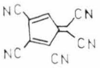
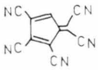
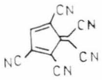
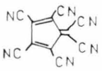
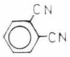
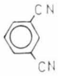
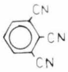
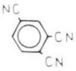
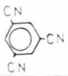
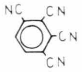
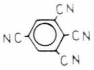
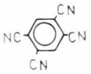
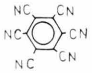
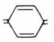
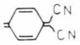
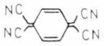
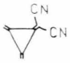
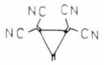
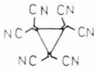
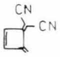
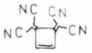
Systems	Point group	AEA [eV]	$-E_{\text{LUMO}}$ [eV]	IP [eV]
Ethylene				
	D_{2h}	−1.019	−1.320	10.177
	C_s	0.328	−0.026	10.617
	C_{2v}	1.384	0.891	10.997
	C_{2v}	1.407	0.985	10.945
	C_{2h}	1.438	1.015	10.965
	C_s	2.303	1.792	11.251
	D_{2h}	3.056	2.498	11.484
Fulvene				
	C_{2v}	2.450	1.875	9.788
	C_s	2.921	2.301	10.115
	C_s	2.994	2.368	10.182
	C_s	3.406	2.773	10.417
	C_s	3.433	2.765	10.443
	C_{2v}	3.369	2.718	10.383
	C_{2v}	3.456	2.796	10.492
	C_s	3.832	3.159	10.702
	C_s	3.815	3.147	10.660
	C_{2v}	4.193	3.508	10.883
Benzene				
	D_{6h} [1]	−0.090	−0.367	9.389
	C_{2v}	0.874	0.514	9.816
	C_{2v}	1.551	1.126	10.194
	C_{2v}	1.470	1.604	10.216
	C_{2h}	1.671	1.253	10.182
	C_{2v}	1.998	1.515	10.550
	C_s	2.178	1.716	10.526
	D_{3h} [1]	1.878	1.455	10.630

Table 2. (continued)

Systems	Point group	AEA [eV]	$-E_{\text{LUMO}}$ [eV]	IP [eV]
	C_{2v}	2.541	2.040	10.817
	C_{2v}	2.618	2.103	10.855
	D_{2h}	2.711	2.234	10.785
	C_{2v}	3.016	2.498	11.094
	D_{6h} [1]	3.270	2.750	11.347
p-Dimethylenequinone				
	D_{2h}	0.899	0.531	8.189
	C_{2v}	2.336	1.808	8.950
	C_{2h}	3.421	2.801	9.430
Trimethylenecyclopropane				
	D_{3h}	0.529	0.197	9.416
	C_{2v}	2.008	1.514	10.113
	C_{2v}	3.066	2.502	10.564
	D_{3h}	3.899	3.320	11.080
Dimethylenecyclobutane				
	C_{2v}	0.274	−0.376	9.520
	C_s	1.806	1.125	9.802
	C_{2v}	2.597	1.924	10.433

[1] The point group of anion was reduced to C_{2v}.

not used in the correlation analysis. The incorrectness may be connected with the experimental difficulties in the identification of the transition from and to the lowest vibrational states of the neutral molecule and its anion. An estimation of the correct value of TCNE would be very important, for example in the investigation of EDA (electron donor-acceptor complexes) in which TCNE is a very effective electron acceptor.

Dependence of the AEA on the energy of LUMO and HOMO

The calculated AEA, first IP, and LUMO energies of cyano derivatives of ethylene, benzene, fulvene,

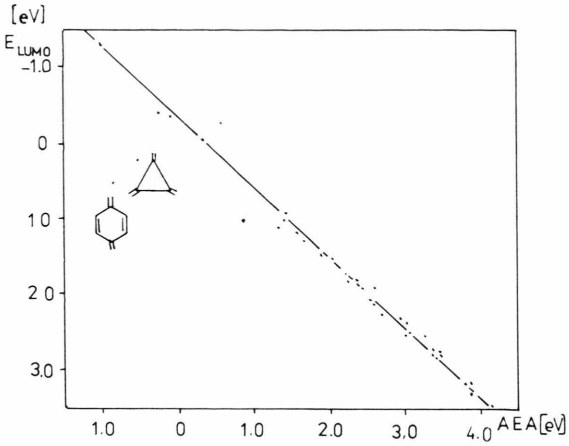


Fig. 2. Correlation of AEA_{MNDO} with E_{LUMO} of the compounds given in Table 2.

p-dimethylenequinone trimethylenecyclopropane and dimethylenecyclobutane are given in Table 2 together with the point groups which were used as the symmetry restrictions in the optimization of the geometry of the neutral molecules. Due to the Jahn-Teller effect the symmetry of the anions of benzene, 1,3,5-tricyanobenzene and heksacyanobenzene was lowered from that of D_{6h}, D_{3h}, and D_{6h} to C_{2v}. Addition of an electron to the ethylene derivatives causes the C=C bond to lengthen by about 0.05 Å, and it appears that the molecule expands after the addition of the electron. Indeed, proportionality between the energies of LUMO orbitals and AEA (both found by MNDO) is not expected (Koopman's theorem is not realized). However, these two values correlate very well, as illustrated in Fig. 2, and the equation is $AEA = -1.078\ LUMO + 0.387$, $R = 0.9979$ for 40 points; standard deviation = 0.052 eV) found by the least squares method. If the correlation is limited to one system, then it becomes better, without a change of the slope. If the change of the intercept in the equation is assumed to be a measure of the energy of reorganization of electrons of the neutral molecule after addition of an extra electron, then it is clear that this energy depends to some extent on the system considered. For benzene, p-dimethylenequinone and trimethylenecyclopropane cyano derivatives the shift is 0.33 eV, for fulvene cyano derivatives 0.47 eV, for methylenecycloheptatriene cyano derivatives 0.60 eV, and for dimethylenecyclobutane cyano derivatives 0.65 eV. Estimation of the AEA of TCNE by the correlation equation gives 2.5 eV, which is equal to the value obtained by MNDO, and is very close to the average from the two experimental values too. Hence both experimental determinations (Table 1) seem to be encumbered with error.

Many efforts have been made to correlate experimentally difficult to obtain AEA's and much more

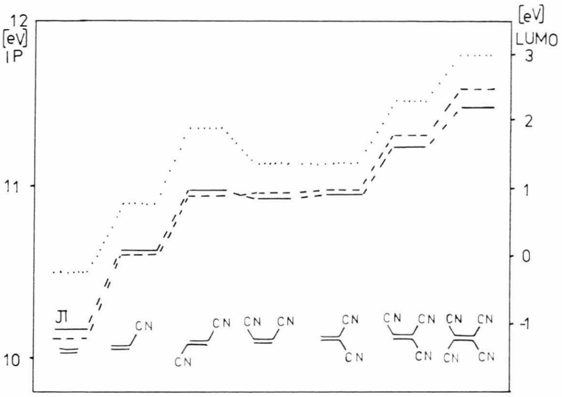


Fig. 3. The changes of the calculated (——) and experimental (---) ionization potentials, and changes of E_{LUMO} (...) depending on the number of cyano substituents in ethylene.

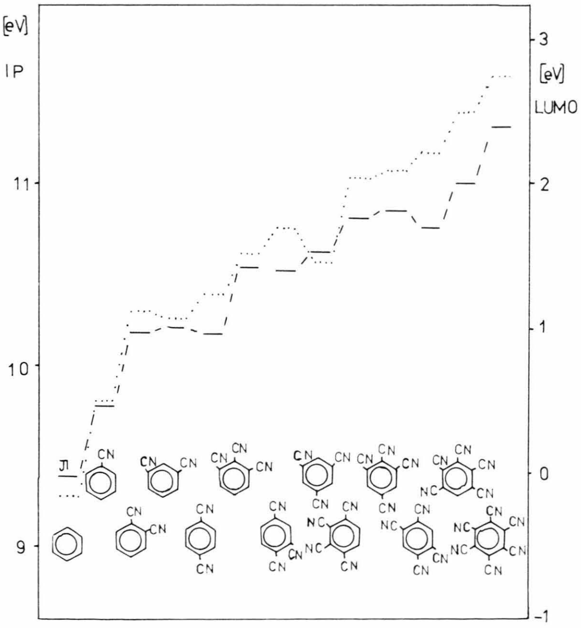


Fig. 4. The changes of the calculated ionization potentials (——) and E_{LUMO} (...) depending on the number of cyano substituents in benzene.

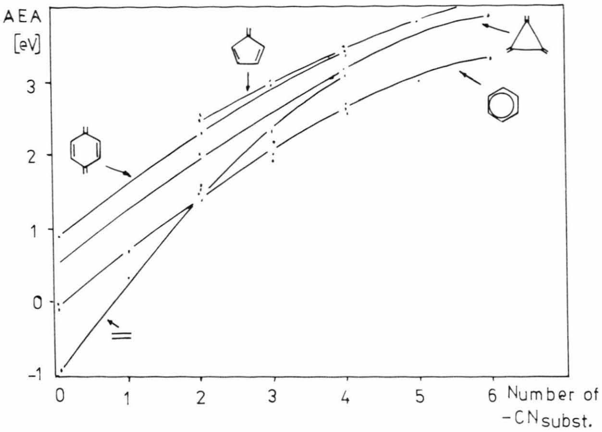


Fig. 5. The change of the adiabatic electron affinity with the number of cyano substituents.

accessible IP's [13]. Houk and Munchausen [2d] claim that on the basis of STO-3G a HOMO and LUMO correlation can be observed and hence, assuming Koopmans theorem, a correlation of EA and IP. Even if such a correlation is possible within closely similar compounds, for example cyano derivatives of benzene of fulvene etc..., the results obtained on the MNDO level show no correlation for cyano derivatives of unsaturated hydrocarbons. The correlation coefficient of the equation $EA = a\,IP + b$ for 40 investigated compounds was only 0.4424.

Dependence of AEA and IP on the number of cyano substituents

Table 2 shows a monotonic change of AEA and the first IP with increasing number of cyano substituents within one class of compounds, for example benzene and its derivatives. The interaction of the cyano substituent with double bonds is inductive and conjugative in character. Inductive effects lower the energy of both frontal orbitals, HOMO and LUMO, whereas conjugative effects of the $C{\equiv}N$ π-orbital and $C{=}C$ π-orbitals lower energy of LUMO and rise energy of HOMO, Figs. 3 and 4. The AEA values increase with the increasing number of cyano substituents, Fig. 5, and there is no linear correlation between the number of the cyano substituents present in the system and AEA. The change brought about by succeeding cyano groups is almost the same for all investigated systems except for ethylene.

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