

## Potential Energy Surfaces Calculations for Ionpairs (Part 1). A Comparison of Peacock and Simonetta Method

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(Received 26th September, 1992, revised 7th November, 1992)

**Summary:** In order to study the efficacy of Peacock method, potential energy surfaces calculations were carried out on Naphthalene (molecule, anionradical and dianion) and p-dicyanobenzene a (anion radical) Peacock method. The results obtained were compared with those from Simonetta method. It was found that as regards the structure of ionpairs, both methods give the same results for conjugated hydrocarbons. Some molecular plane potential surface calculations were carried out for tetraphenylethylene (Neutral, anion radical and dianion).

### Introduction

Ionpairs are a class of chemical entities, very much relevant with reference to polymerization and electron transfer process [1-2]. This is specially true for ionpairs derived from the substituted ethylenes by alkali metal reduction [3-4]. Theoretical information regarding the structure of ionpairs can be obtained from the study of potential energy surfaces [5-7]. It must however be noted that calculation of potential energy surfaces have generally been confined to the ionpairs derived from anions (or anion radicals) and a cation, but not a dianion and a cation or a dianion and a dication [6-7]. An investigation has thus been undertaken to make a systematic study on the structure of ion pairs particularly dianion-cation and dianion-dication pairs, through potential energy surfaces calculations. The dianion-alkali metal cation and dianion-alkaline earth dication ionpairs e.g. those derived from substituted ethylene by alkali metal or alkaline earth metal reduction are worth investigating as they play an important role in polymerization through disproportionation.

Potential energy mappings are carried out using various methods [8-13]. However, here the efficacy of two methods (a) Peacock's [14-15] and (b) Simonetta's [5] are presented. Calculations and mappings are carried out on Naphthalene (molecule, anion radical and dianion), ortho, meta and para dicyano benzene (anion radicals) and tetraphenylethylene (molecule, anion radical and dianion) by the above mentioned methods and results obtained.

### Methods

The electrostatic potential  $v(r)$  created at a point  $r$  in the space around a molecule by nuclei and electrons is given by [5]

$$v(r) = \int \frac{e(r_1) dr_1}{|r_1 - r|} + \sum_A \frac{Z_A}{|R_A - r|}$$

where  $Z_A$  is the charge on the nucleus the located at  $R_A$  and  $e(r)$  is the electron density charge distribution function of the molecule. As stated above Eq (1) is the rigorous definition of the electrostatic potential, the sophistication in the calculated numerical value of which depends upon the sophistication in the calculation of  $e(r)$ . For calculation of  $e(r)$  molecular orbital methods-Huckel, w-technique, McLachlan and self consistent field in various prescription (including ab initio) are used.

#### 1. Peacock method [14-15]

Peacock proposed a very simple expression for the calculation of potential energy contours. The method though initially proposed for pi-electron molecules, has not been as extensively used as it should have been, nor its full potentiality has been explored. The details of the method are given below.

The potential energy of a unit positive charge moving in the field of a molecule may be represented by [14]

$$V = (\delta_{rs} - q_{rs})/R_{rs} \quad (2)$$

Where  $R_{rs}$  is the distance between the point charge and the centroid of the bond  $rs$  (or the atom if  $r = s$ ) and  $q_{rs}$  is the atom charge or overlap charge (for  $r = s$  and  $r \neq s$  respectively).  $\delta_{rs}$  is the Kronecker delta and in fact is the framework ion charge in atomic units for an atom which contributes one pi electron to the pi system. It is assumed that each framework ion may be regarded as a point positive charge. The approximation hold at distances which are large enough for polarization effect to be negligible.

The atom charge ( $q_{rr}$ ) and the overlap charge ( $q_{rs}$ ) can be described at the amount of charge localized in the orbital region

$$\begin{aligned} q_{rr} &= p_{rr} \\ q_{rs} &= 2p_{rs} S_{rs} \end{aligned} \quad (3)$$

where  $p_{rr}$  and  $p_{rs}$  are the deorthogonalized charge densities and bondorders and  $S_{rs}$  is the overlap between the atoms and  $s$ . The overlap between  $2p_z$  atomic orbital is given by

$$S = \exp(-w/2) [1 + W/2 + W/10 + W/120]$$

where  $w = Zr$ ,  $Z$  being the effective nuclear charge and  $r$  the internuclear distance in atomic units. The rest of the detail is given in ref. [14].

## 2. Simonetta method [5]

Simonetta used essentially eq. (2) given above which in LCAO-MO approximation transforms into

$$V(r) = -\sum_r \sum_s P_{rs} \int \frac{U_r(r) U_s(r)}{|r-r_A|} + \sum \frac{Z_A}{|r-r_A|}$$

$$\text{where } P_{rs} = 2 \sum C_{ri} C_{si} \quad (6)$$

$U_p$  and  $U_r$ 's are the atomic orbitals and  $P_{rs}$  is the bondorder.

## Results and Discussion

Calculations using Peacock and Simonetta methods were carried out on the following systems

- Naphthalene molecule, anion radicals and dianion
- ortho, meta and para isomers of Dicyanobenzene (anion radicals)
- Tetraphenylethylene anion radical and dianion

Peacock [14] had carried out calculations on Naphthalene molecule while Simonetta [5] carried out calculations on Naphthalene and p-Dicyanobenzene anion radicals. Calculations were carried out in the molecular plane as well as in planes parallel to the molecular plane.

### (a) Naphthalene

Molecular plane potential energy calculations by both methods, Peacock as well as Simonetta were carried out. It was found that in both the models, the minimum potential energy decreases (becomes more negative) from the neutral molecule to anion radicals to dianions (Table 1 and fig. 1). It was also observed for a neutral molecule, in the

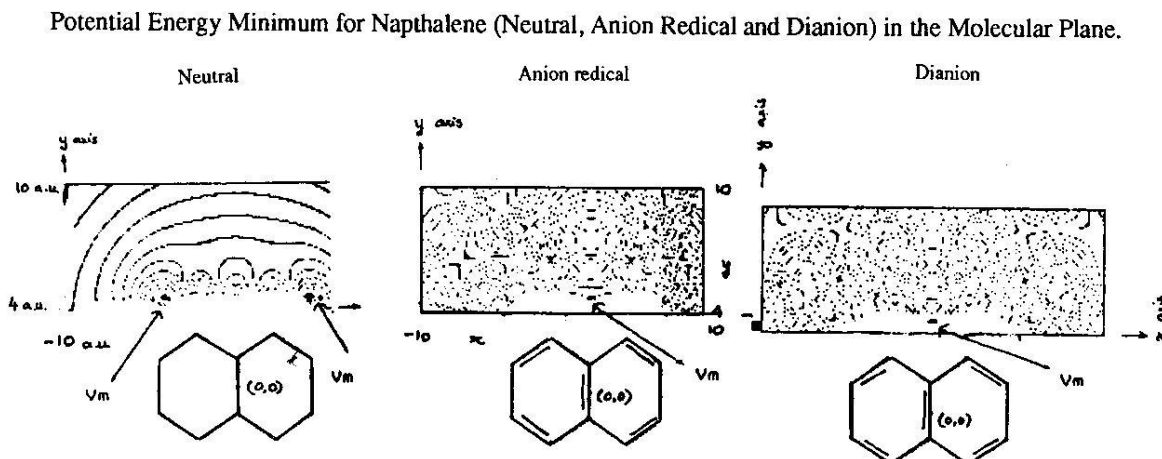


Fig. 1: The isocenergetic contours were drawn using the software developed for this work.

Table 1: Minimum potential energies for Naphthalene in the molecular plane

Species	a Vm (a.u)	b X (A°)	c Y (A°)
Neutral	-0.02	5	4.3
Anion	-0.244	0	4.7
Dianion	-0.468	0	4.5

(a) Vm is the minimum potential energy in the molecular plane. (b), (c) are the coordinates of the point of minimum potential energy. In the molecular plane the potential energy is calculated with Y 74 A°

specified range and magnification, well defined contours were obtained while for dianions the contours were not well defined.

The potential energy contours in planes parallel to the molecular plane for naphthalene anion radical are more illustrative (fig. 2). Potential energy scanning in the plane 1.5 Å above the molecular plane indicate the existence of two minima curves, whereas, only one minimum curve exists at a height of 2.5 Å and above (see Table 2). Simonetta's calculations predict a similar location of the minima. The results of these calculations lead to the conclusion that Peacock and Simonetta's method are equivalent as they give minima at the same point in space, the difference in the absolute values of potential energies notwithstanding. It is particularly satisfying to extend the use of Peacock

method to the charged species and to see results obtained by this method qualitatively agreeing with these obtained by Simonetta [6]. Also since in an ionpair, as a first step, it is the position of the metal cation in the vicinity of the anion which is of primary interest, it does not matter how deep is the potential minimum in absolute terms. Structures of the metal cation - naphthalene anion radical is predicted to be the same by both the methods.

#### (b) Dicyanobenzene

Calculations were carried out on the anion radicals of all the three isomers-ortho, meta and para dicyanobenzenes. The anion radical is of particular interest, primarily because Simonetta [5,16] has also, carried out calculations on the anion radi-

Table 2: Comparison of potential energy minimas for Naphthalene

Coordinates	(Anion Radical) Potential energies					
	Peacock's method			Simonetta's method		
a Z (A°)	b X (A°)	c Y (A°)	d Vm a.u.	e Vm Kcal/mole	f Vm a.u.	g Vm Kcal/mole
0°	4.7	0	-0.244	-153.0	-	-
	1.212	0				
1.5 (2.83 a.u.)	-1.212	0	-0.271	-169.7	-0.207	-130
2 (3.78 a.u.)	0	0	-0.207	-129.7	-0.166	-104
2.5 (4.72 a.u.)	0	0	-0.183	-115.0	-0.148	-93

(a), (b) and (c) a, b and c are the coordinates of the point at which V is calculated. (a) Z coordinate gives the height above the molecular plane. (b), (c) The molecular plane is taken as the XY plane, and the centre of the molecule is taken as the origin (0,0,0). (d) Vm is the minimum potential energy in the given plane (using Peacock's method). (e) Z=0 signifies the molecular plane. In this plane, V is calculated with Y > 4A°. (f) Minimum potential energy from Simonetta's model. (see ref. 5) (g) In these calculations r(C-C) = 1.4 A°

Potential energy curves for anion radical of naphthalene.  
(in planes parallel to the molecular plane)

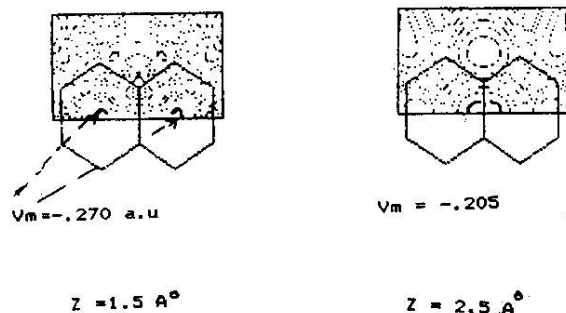


Fig. 2: Z indicates the height above the molecular plane.

calcs and experimental ESR data are available for comparison.

Simonetta reported two absolute minima in the molecular plane at  $1.5 \text{ \AA}$  ( $1.5 \text{ \AA}$  is the minimum distance between the cation and any one of the atomic centres) from the nitrogen atom. A relative minimum was also reported to be present in the plane  $1.5 \text{ \AA}$  above the benzene ring. These results, however, do not agree with the results obtained by Peacock method using unrestricted Hartree Fock (UHF-SCF MO method). This method predicts a minimum in a plane  $1.5 \text{ \AA}$  above the molecular plane. Results are tabulated in Table 3 and 4. Minimum energy curves can be seen in figs. 3 and 4. Another anomaly was also observed for the ortho isomer. Existence of two minima were reported [16] starting at a distance of  $2 \text{ \AA}$  from the anion by Simonetta and Cremaschi. Peacock's method predict only a single minimum energy curve starting

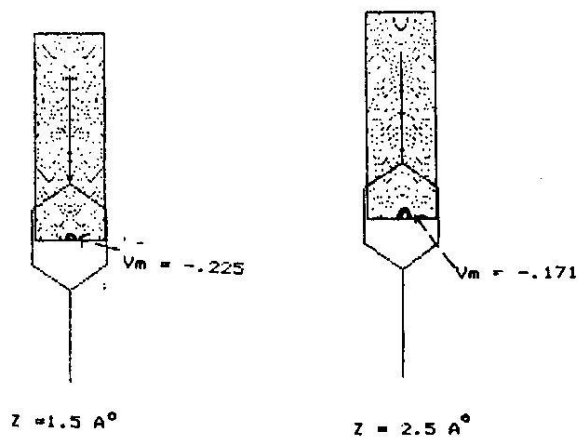


Fig. 3: Potential energy curves for anion radical of p-dicyanobenzene.

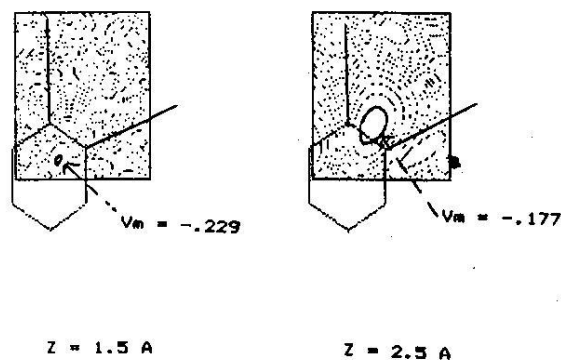


Fig. 4: Potential energy curves for anion radical of o-dicyanobenzene

Table 3: Comparison of potential energy minimas for p dicyanobenzene

Coordinates			(Anion Radical)			
Z	X	Y	Potential Energies			
			Peacock's method		Simonetta's method	
(A)	(A)	(A)	d	d	f	f
			Vm	Vm	Vm	Vm
			a.u.	Kcal/mole	a.u.	Kcal/mole
0 <sup>e</sup>	0	5.7	-0.175	-109.812	-0.199	-125.000
1.5	0	0	-0.225	-141.2	-0.178	-112
(2.83 a.u.)						
2	0	0	-0.193	-121.1	-	-
(3.78 a.u.)						
2.5	0	0	-0.171	-107.3	-	-
(4.72 a.u.)						
3	0	0	-0.151	-94.75	-0.132	-83
(5.67 a.u.)						

(a) - (e) see footnotes of Table 2 (f) Minimum potential energy from Simonetta's model (see ref. 16)

Table 4: Comparison of potential energy minima for m-dicyanobenzene

Coordinates			(Anion Radical)			
			Potential energies			
			Peacock's method		Simonetta's method	
a	b	c	d	d	f	f
Z	X	Y	V <sub>m</sub>	V <sub>m</sub>	V <sub>m</sub>	V <sub>m</sub>
(A°)	(A°)	(A°)	a.u.	Kcal/mole	a.u.	Kcal/mole
0°	0	5.7	-0.157	-98.52	-0.202	-127
1.5	0	0	-0.184	-115.5	-0.180	-113
(2.83 a.u.)						
2	0	0	-0.158	-99.1	-	-
(3.78 a.u.)						
2.5	0	0	-0.139	-87.2	-	-
(4.72 a.u.)						
3	0	0	-0.125	-78.43	-0.132	-83
(5.67 a.u.)						

(a)-(e) see footnotes of Table 2 (f) Minimum potential energy from Simonetta's model (see ref. 16) (g) In the above calculations r(C-N) = r(C-C) = 1.4 Å°

from a distance of 2Å° for all the three isomers. This point needs to be investigated further.

Calculation of Naphthalene and p-dicyanobenzene have established the qualitative agreement between the results obtained from Peacock and Simonetta methods for aromatic hydrocarbons only. For heteroaromatics no agreement was observed.

#### (c) Tetraphenyl ethylene

Since the ultimate goal is to carry out thorough calculations on the anion radical and dianion derived from substituted ethylenes, some molecular plane calculations were carried out for tetraphenyl ethylene molecule, anion radical and dianion using Peacock method (Table 5).

Though quantitative values of potential energy minima are desirable e.g. to have a measure of barrier heights, nevertheless, the position of minima can give insight into the location of cations, say, ionpairs, M<sup>+</sup>, φ<sub>4</sub>ET<sup>+</sup>, [M<sup>+</sup>φ<sub>4</sub>ET<sup>+</sup>]<sup>-</sup> and M<sup>+2</sup>φ<sub>4</sub>ET<sup>-2</sup> (where M = alkali or alkaline earth metal) and φ<sub>4</sub>Et is tetraphenyl ethylene. The optical spectra as is the case ESR spectra will also be affected by the proximity of these cations with respect to anions. This is well documented in the case of tetraphenylethylene dianion with alkali metal cation as counter ions [4].

Table 5: Comparison of potential energy minimas for tetraphenylethylene

Coordinates				
a	b	c	d	d
Z	X	Y	V <sub>m</sub>	V <sub>m</sub>
(A°)	(A°)	(A°)	a.u.	Kcal/mole
Anion radical				
1.5	0	0	-0.350	-219.6
(2.83 a.u.)				
2	0	0	-0.305	-191.4
(3.78 a.u.)				
2.5	0	0	-0.275	-172.6
(4.72 a.u.)				
3	0	0	-0.243	-152.5
(5.67 a.u.)				
Dianion				
1.5			-0.477	-299.5
(2.83 a.u.)				
3.78			-0.425	-266.7
(a.u.)				
2.5			-0.383	-240.3
(4.72 a.u.)				
3			-0.348	-218.4
(5.67 a.u.)				

(a)-(d) see footnotes of Table 2.

These calculations establish that for studying the structure of ionpairs i.e. locating the proximity of cation in an ionpair. M<sup>+</sup> X<sup>-</sup> molecular electrostatic potential calculated by Peacock method is as good as the more sophisticated Simonetta method for aromatic hydrocarbons.

#### Acknowledgement

The present work was supported by Pakistan Science Foundation. The author is indebted to Dr.

M. Mohammad, Dr. A.Y. Khan and D. S. Subhani for their guidance, help and advise.

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