
ATTI ACCADEMIA NAZIONALE DEI LINCEI
CLASSE SCIENZE FISICHE MATEMATICHE NATURALI
RENDICONTI

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**An ab initio Calculation of the Structure of
Naphthalene Ion Pairs**

*Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche,
Matematiche e Naturali. Rendiconti, Serie 8, Vol. 60 (1976), n.4, p. 476–482.*

Accademia Nazionale dei Lincei

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Chimica. — *An ab initio Calculation of the Structure of Naphthalene Ion Pairs.* Nota di PIETRO CREMASCHI, ALDO GAMBA (*), GABRIELE MOROSI e MASSIMO SIMONETTA (**), presentata (***) dal Socio M. SIMONETTA.

RIASSUNTO. — Le superfici potenziali dell'anione naftalene sono state calcolate con il metodo *ab initio* e con il formalismo del potenziale elettrostatico molecolare, includendo anche l'effetto del solvente.

La forma di queste superfici permette di interpretare e di razionalizzare la struttura delle coppie ioniche con i cationi alcalini.

INTRODUCTION

The metal hyperfine splitting (hfs) constants observed in esr spectra of radicals obtained by reduction with alkali metals in aprotic solvents prove the existence of ion pairs [1]. The dependence of the size and of the sign of these constants upon temperature has been used to measure kinetics and equilibria between different ion pairs. Experimental findings have been rationalized through proper models [2, 3] which imply the knowledge of the geometry of the ion pairs.

The ion pairs formed by reduction of naphthalene with alkali metals have been studied in different solvents by many Authors [1], both experimentally and theoretically. Only semiempirical calculations have been performed on this system by using the Huckel-McClelland [4] and the INDO [5] methods. The former, applied to the naphthalene⁻/Na⁺ ion pair, predicts two minima, over the centre of the rings, separated by a very small barrier. INDO calculation suggests the most stable positions for Li⁺ over the centre of the rings, while, for the Na⁺ ion pair, convergence difficulties have prevented the study over the individual rings.

However the Huckel-McClelland method is rather crude, and the INDO results are perhaps not too meaningful due to the overlap inadequacies of the method [5].

An *ab initio* calculation explicitly including the two counter ions should be a better approach. We found in the literature one example of this kind of calculation, namely the pyrazine⁻/Li⁺ ion pair [6]. However the extension to a larger system such as naphthalene⁻/Li⁺ would be an excessively cumbersome and expensive project.

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(***) Nella seduta del 10 aprile 1976.

In an attempt to find a less sophisticated but still reliable approach, we have verified [7-10] that the electrostatic potential, evaluated by using an *ab initio* wave function of the anion, can be successfully used to study the structure of ion pairs. We have also found that the shape of the potential surface is not modified either by enlarging the basis set or by using quartet spin component annihilated wave functions [9].

In view of this in the present paper we study the potential of the naphthalene anion to investigate the structure of ion pairs of the naphthalene with alkali metals.

CALCULATIONS

The *ab initio* wave functions of the neutral molecule and of the radical anion have been calculated by the GAUSSIAN 70 program [11] using a STO-3 G minimal basis set [12]. The unrestricted method of Pople and Nesbet [13] has been used for the open shell system.

The same planar model geometry has been assumed for the neutral molecule and its ion: $r(\text{C}-\text{C}) = 1.4 \text{ \AA}$, $r(\text{C}-\text{H}) = 1.08 \text{ \AA}$ and 120° for all bond angles.

In the case of the radical anion the influence of the solvent has been studied through the model of Klopman and Germer [14-16], who simulate the first shell of solvation through a number of induced "solvatons". A solvaton is associated with each atomic centre and carries a charge equal to the opposite of the Mulliken net charge of the associated atomic centre. As we are dealing with an anionic species, the solvaton charge has been modified [8] by adding the value of q/N to each solvaton, where q is the ion charge in a.u. and N is the number of atoms.

The calculations were performed *in vacuo* and in solvents of low dielectric constant such as dimethoxyethane (DME), a commonly used solvent in esr ion pair studies. The density matrices were used to obtain the electrostatic interaction energy of the anion radical with a unit positive charge [17].

Potential surfaces were calculated in the distance range $1.5-3 \text{ \AA}$ from the radical. These distances have been chosen as they can represent approximate limit values of the regions accessible to the alkali cations [4, 7, 18]. In this model the hard sphere approximation is used for the cation and the distance of the minimum approach depends on the size of the cation.

The isotropic hyperfine coupling constants of ^{13}C and ^1H have been evaluated in the standard way through the equation:

$$(1) \quad a_N = \frac{8}{3} \pi g \beta \gamma_N \hbar \sum_m^{\text{orb.}} \sum_n^{\text{orb.}} (P_{mn}^\alpha - P_{mn}^\beta) \chi_m(0) \chi_n(0)$$

where: g is the electron g factor; β is the Bohr magneton; γ_N is the gyromagnetic ratio of nucleus M ; $P^\alpha - P^\beta$ is the difference between α and β density matrices.

The wave functions before and after quartet component spin annihilation [19, 20] were used.

RESULTS AND DISCUSSION

We have performed an *ab initio* calculation on the naphthalene anion: as there are no other *ab initio* results on this system, to test the reliability of our wave function we have performed the calculation on the corresponding neutral molecule with the same basis set. Our total energy is -378.6745 a.u., while Buenker and Peyerimhoff [21] obtained -382.7883 a.u. with an extended basis set. This comparison shows that our basis set is rather poor, nevertheless we think that the potential surfaces obtained by our wave function are reliable, as we have verified in a previous study [9] that the extension of the basis does not significantly change the shape of the potential surface.

Anion net charges, calculated *in vacuo* and in DME, are shown in Table I.

TABLE I.

Net charges of the naphthalene anion.

Atom	<i>In vacuo</i>	In DME
C ₁	-0.1132	-0.1149
C ₂	-0.1369	-0.1348
C ₉	-0.0014	$+0.0329$
H ₁	$+0.0008$	-0.0078
H ₂	0.0000	-0.0089

The charge distribution of the radical anion is slightly modified by the inclusion of the solvent perturbation. This result suggests that the shapes of the potential *in vacuo* and in solvents of low dielectric constant should be very much alike. The actual calculations *in vacuo* and including solvent interaction confirm this behaviour, so, without any loss of generality, we report only the potential surfaces of the radical anion in solution.

The maps of the electrostatic potential in planes 1.5 and 3 Å over the radical are shown in figs. 1 and 2. The most significant energy values on lines in a σ_v plane and equidistant from the nearest nuclei of the anion are reported in fig. 3. Assuming that an alkali cation should not come closer to the anion than about 1.5 Å, the region at distances shorter than this value was not considered.

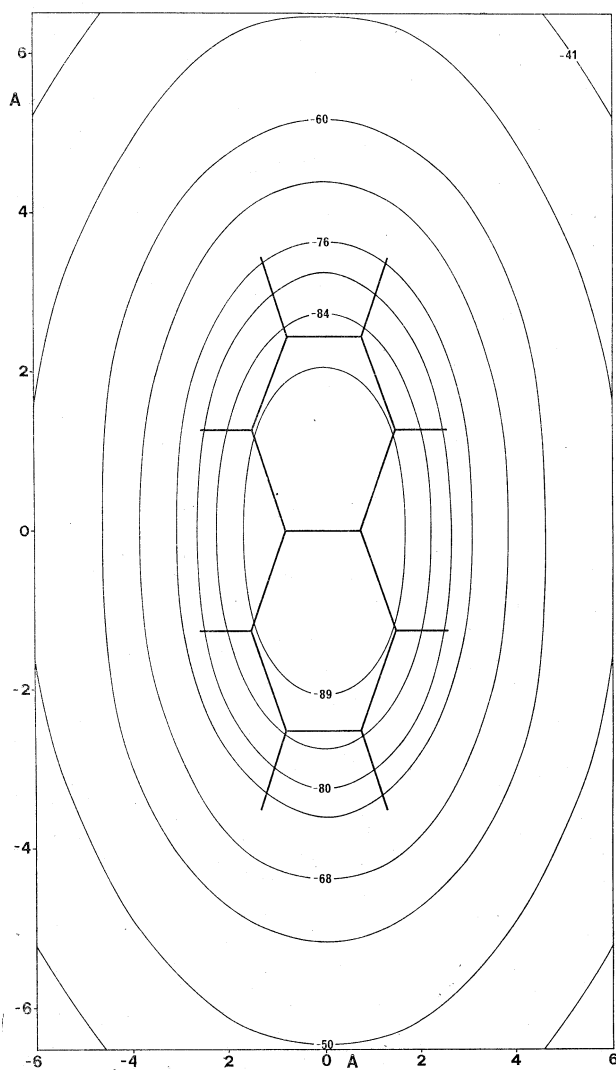


Fig. 1. — Contour lines of the electrostatic interaction energy between a naphthalene anion and a unit positive charge: plane 3 Å over the molecular one.

From the figs. it emerges that two equivalent minima are present in the region nearer to the anion (range 1.5-1.8 Å). A barrier of 13 kcal/mole is found at 1.5 Å over the centre of the molecule. This barrier sharply decreases to zero, and starting from about 2 Å, only one flat minimum is present over the centre of the radical.

The present results suggest that only a small cation could be found in one of the two symmetric wells over the centre of the rings. In order for the spin distribution to have molecular symmetry the cation must jump rapidly from one ring to the other. Indeed Li hfs quartets exhibit line width variations [22, 23], with the outer pair of lines broader than the inner one. This fact has been interpreted as due to intra or intermolecular motional modulations

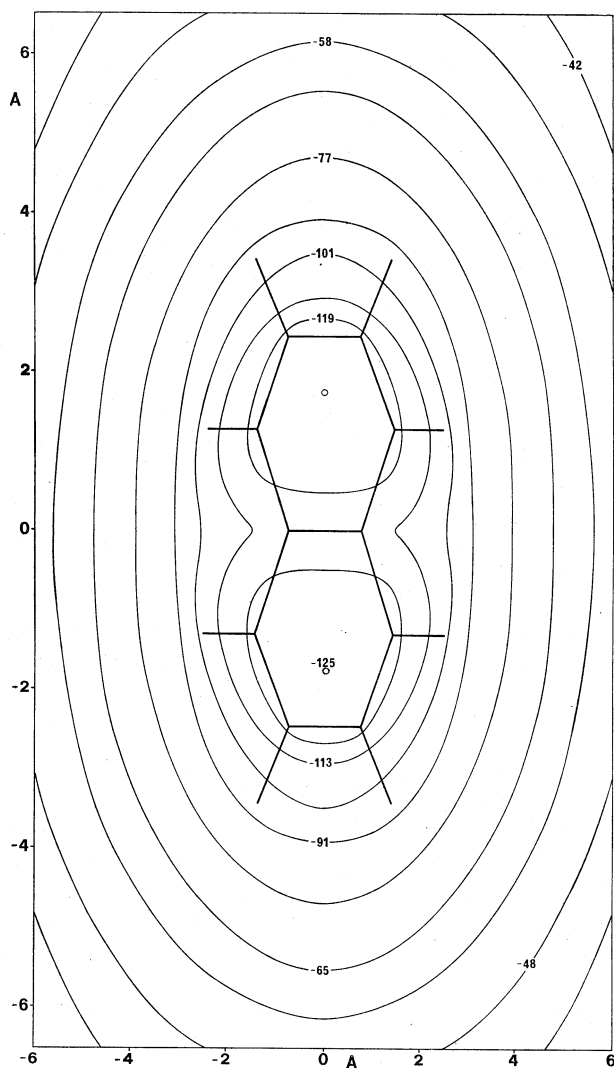


Fig. 2. - Contour lines of the electrostatic interaction energy between a naphthalene anion and a unit positive charge: plane 1.5 \AA over the molecular one.

of the metal splittings [22-24]. Our results are compatible with an intramolecular motion between two sites separated by a low barrier. On the other hand for larger cations or for small cations strongly solvated only one position over the centre of the anion is accessible: indeed no line width alternation has been observed in esr spectra of heavier cations.

The potential well exists at least as far as 10 \AA over the molecular plane, so many vibrational states are likely to be accessible to the cation. This result supports the Atherton-Weissman model [22, 25], which describes the dependence of the metal hfs constants on temperature by considering the vibrations the alkali metal presumably performs in the potential well of the anion.

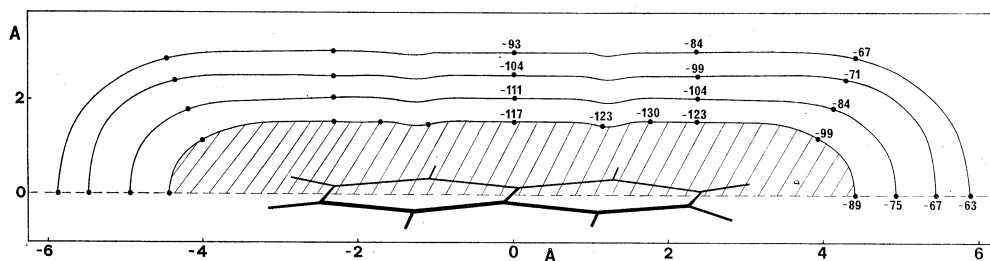
Fig. 3. — Equidistant lines (1.5, 2.5 and 3 Å) in a σ_v plane of naphthalene anion.

TABLE II.

Hfs coupling constants (gauss) before (sd) and after (aa) quartet component annihilation

Atom	a_{sd}	a_{aa}	a_{exp}	Ref.
C ₁	+ 33.13	+ 11.23	7.10	26
C ₂	— 5.95	— 1.98	1.20	27
C ₉	— 21.59	+ 7.16	—	—
H ₁	— 19.94	— 6.29	— 4.90	28
H ₂	— 0.35	— 0.11	— 1.89	28
$\langle S^2 \rangle$	0.880	0.764	—	—

The hfs constants obtained from the *ab initio* wave function with equation (I), before and after quartet component annihilation, are shown in Table II. Both wave functions correctly reproduce the qualitative trend, but the quantitative results are as satisfactory as can be expected with calculations of this type only when a purified wave function from the quartet spin component is used.

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