

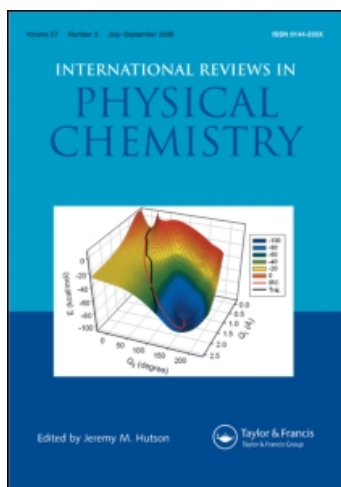
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THE STRUCTURE OF ION PAIRS IN SOLUTION

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ABSTRACT

In the first part of this review ion pairs formed by an alkali cation and an organic paramagnetic anion in ethanol solutions are considered. The molecular potential generated by the charge distribution of the anion is calculated within the electrostatic approximation for a number of aromatic derivatives, most of which contain nitro-groups. From the corresponding maps the most favourable positions for the cations are obtained and the results are compared with information obtainable from ESR spectra of the ion pairs and free anions. In the second part, the dissociation of CH_3F and $\text{C}_6\text{H}_5\text{N}_2^+$ in water is studied by means of a supermolecule model in the frame of the CNDO MO theory. The results are in line with kinetic data and other experimental evidence.

Two different kinds of ion pairs are considered in this review. The first one encompasses ion pairs that form by alkali-metal reduction of suitable organic substrates in ethereal solvents. A radical anion is present in these pairs and they are currently investigated by means of electron spin resonance (ESR) spectroscopy.

Ion pairs of the second type are formed in solvolytic reactions, specially with alkyl halides as reagents. Both ions are here closed-shell systems and kinetics and mechanistic methods are currently used to demonstrate and describe their formation and stability. Though an impressive amount of experimental work (Szwarc, 1972; Winstein, 1965) has been carried out for the two classes of compounds (both paramagnetic and diamagnetic), very little is known of their geometrical structure due to the lack of an appropriate technique. This is the typical situation when experiments must be paralleled by theoretical computations and the problem can only be solved with the help of quantum mechanics. Again, due to the different nature of the ion pairs, different theoretical approaches have to be used, the paramagnetic pairs being investigated by the molecular potential method (Scrocco and Tomasi, 1973) and the diamagnetic ones by the CNDO technique, one of the standard approximations of the molecular orbital method (Pople and Beveridge, 1970).

PARAMAGNETIC ION PAIRS

The electrostatic molecular potential method has been developed as a tool for the prediction of the relative reactivity of functional groups in ionic reactions (Scrocco and Tomasi, 1973). It is based on molecular orbital theory, where a number of approximations are included, namely the Born-Oppenheimer, the self consistent field (SCF), the LCAO (linear combination of atomic orbitals), the Hartree and the electrostatic approximations. The Born-Oppenheimer approximation allows separation of nuclear and electronic motions. The stationary electronic states are found for fixed positions of the nuclei, and the total energy (electronic energy plus nuclear repulsion) is obtained as a function of nuclear

coordinates. In the SCF approximation the wavefunction has the form of a single Slater determinant and for a system comprising two closed-shell subsystems (usually molecules) A and B , it can be written as

$$\Psi_{AB}^{\text{SCF}} = \frac{1}{\sqrt{(2N)!}} \det |\phi_1(\mathbf{r}_1) \alpha_1 \phi_1(\mathbf{r}_2) \beta_2 \dots \phi_N(\mathbf{r}_{2N}) \beta_{2N}|$$

where $2N$ is the total number of electrons, ϕ_i is a molecular orbital, r_i are space coordinates for electron i , and α and β are the usual spin eigenfunctions. The molecular orbitals ϕ_i are given by $\phi_i = \sum_r C_{ir} \chi_r$ where χ_r are atomic orbitals (LCAO approximation). In the Hartree approximation it is assumed that, if the separation between A and B is large enough, the exchange contribution to the energy and the charge transfer between the two molecules can be neglected. That is, the electrons are partitioned into two groups, each one belonging to a single molecule, and the wavefunction becomes the product of two functions, relating to molecules A and B :

$$\Psi_{AB}^{\text{H}} = \Psi_A^{\text{H}} \Psi_B^{\text{H}}$$

In this case Ψ_A^{H} is optimized in the field of molecule B , then Ψ_B^{H} in the field of molecule A , and so on, to convergence. If polarization effects can also be neglected, the electrostatic approximation can be introduced, where only electrostatic effects between the two unpolarizable subsystems A and B described by wavefunctions Ψ_A^0 and Ψ_B^0 are taken into account. Then we have

$$\Psi_{AB}^0 = \Psi_A^0 \cdot \Psi_B^0$$

and the interaction energy is given by

$$\begin{aligned} W_{AB} = E_{AB}^0 - E_A^0 - E_B^0 = & -2 \sum_i \sum_{\beta}^B \left\langle \phi_{iA}^*(1) \phi_{iA}(1) \left| \frac{Z_{\beta}}{r_{i\beta}} \right. \right\rangle \\ & - 2 \sum_j \sum_{\alpha}^A \left\langle \phi_{jB}^*(1) \phi_{jB}(1) \left| \frac{Z_{\alpha}}{r_{1\alpha}} \right. \right\rangle \\ & + 4 \sum_i \sum_j \langle \phi_{iA}^*(1) \phi_{iA}(1) | \phi_{jB}^*(2) \phi_{jB}(2) \rangle \\ & + \sum_{\alpha}^A \sum_{\beta}^B \frac{Z_{\alpha} Z_{\beta}}{R_{\alpha\beta}} \end{aligned} \quad (1)$$

where i and j run over the electrons and α and β over the nuclei of subsystems A and B respectively, and the symbols have their usual meaning (McWeeny and Sutcliffe, 1969). W_{AB} represents the interaction energy between the potential field V_A arising from the charge distribution $\gamma_A(\mathbf{r}_1)$ and the second charge distribution γ_B . Usually A is taken to be the more complex of the two molecules. It may be useful to approximate γ_B by a set of point charges q_{kB} located at positions \mathbf{k} . Then the interaction energy becomes

$$W_{AB} = \sum_{\mathbf{k}} V_A(\mathbf{k}) q_{kB}(\mathbf{k})$$

If system B happens to be a monoatomic monovalent cation in position \mathbf{k} , then W_{AB} reduces to

$$W_{AB} = V_A(\mathbf{k}) \quad (2)$$

$V_A(\mathbf{r})$ is easily obtained from the electron charge distribution of molecule A , $\rho_A(\mathbf{r}_1)$, in the form

$$V_A(\mathbf{r}) = - \int \frac{\rho_A(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r}_1 + \sum_{\alpha} \frac{Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|}$$

In the LCAO approximation this equation transforms to

$$V_A(\mathbf{r}) = - \sum_r \sum_s P_{rs} \int \frac{\chi_r^*(\mathbf{r}_1) \chi_s(\mathbf{r}_1)}{|\mathbf{r} - \mathbf{r}_1|} d\mathbf{r}_1 + \sum_{\alpha} \frac{Z_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|}$$

where

$$P_{rs} = 2 \sum_i C_{ri} C_{si}$$

It has been found by experience that molecular orbitals to be used in connection with these calculations must be of 'ab initio' quality, at least at the STO 3G level (Pople and Beveridge, 1970).

Of course the use of the electrostatic molecular potential method in the study of reactivity is highly questionable since, when the two parts A and B come close enough to react, most, if not all, of the approximations in the theory become untenable. This is not the case for ion pairs. Here the cation (usually an alkali-metal cation) and the radical anion, once formed, do not react at all. It is reasonable then to assume that the cation locates itself at the position of the absolute minimum of the potential generated by the anion. Since we use a unit point charge to represent the cation, it must be verified that the minimum is not too close to the anion. We use here the hard-core approximation, that is we exclude that part of the space where strong repulsive forces between the electrons of the two ions arise.

One further point has to be made. The theory so far developed assumes A and B to be closed-shell systems. Now this is true for monovalent alkali cations but it is certainly not for a radical anion where an unpaired electron is present. However, we can still use an unrestricted Hartree Fock (UHF) calculation to obtain the molecular orbitals and the charge distribution of the anion. Of course the wavefunction is now spin-contaminated due to the use of different molecular orbitals for different spins. This point has been checked by performing calculations of the molecular potential surfaces for a number of organic radicals, with and without annihilation of the quartet component of the ground-state wavefunction (Cremaschi *et al.*, 1976a). The potential surfaces were practically unaffected by the projection operation. It has also been verified on the same radicals that the use of an extended basis set (namely the 4-31 G basis (Ditchfield *et al.*, 1971) leads to the same shape of the potential surface and where more minima are present their relative order of stability is preserved. It has also been verified that the point-charge approximation for the alkali cations is well founded: when the interaction energy within the ion pair was evaluated including both the cation and the anion electrons, that is using formula (1) instead of (2), the general shape of the potential surface and the position of the minimum were unchanged, though the absolute energy values were different (Fig. 1).

Another problem in the study of the structure of ion pairs is the influence of the solvent. The inclusion of solvent effects in theoretical investigations should be made easier by the fact that ESR correlation times indicate that it is an average interaction, rather than a specific one. So the solvation model, as proposed by Klopman (1967) and developed by Germer (1974) can be appropriate here. In this model the solvent is represented by a number of induced solvatons, where one solvaton is associated with each atomic centre s

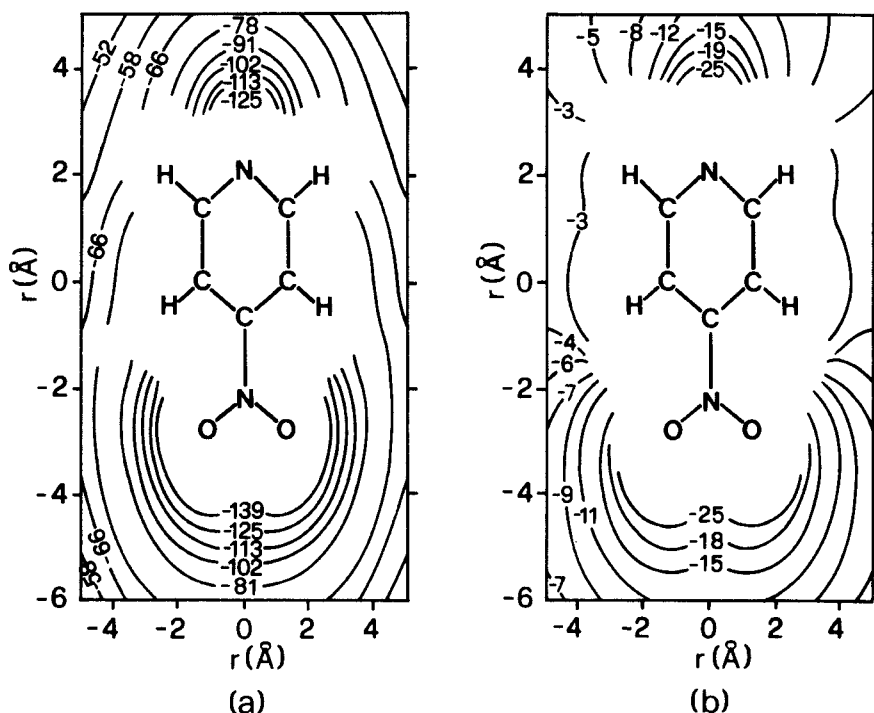


FIG. 1. Isoenergetic contour lines for 4-nitropyridine anion (a) calculated by formula (1); (b) calculated by formula (2).

and carries a charge Q_s equal to the opposite of the net charge on the associated centre, calculated according to the Mulliken prescription. Since we are dealing with charged species, a charge q/N must be added to each solvaton, where q is the ion charge and N the number of solvaton. A perturbed Hamiltonian is used in the SCF procedure, where electron/solvaton and nuclear/solvaton interactions are included. As to the geometry of the radical anion, the experimental geometries for the related neutral molecules can be used, when available, or assumed geometries can easily be set up starting from standard bond lengths and bond angles. The solvaton are placed at a distance equal to the Van der Waals radius when associated with atomic orbitals on the same centre, otherwise at the nuclear centre. We considered only solvents of low dielectric constant, such as tetrahydrofuran and dimethoxyethane, since these are the usual solvents in ESR spectroscopic studies of ion pairs.

It turns out that charge and spin distribution on the radicals *in vacuo* and in the presence of solvent are very similar, so that the molecular electrostatic potential is scarcely affected.

As a first example of theoretical structure determination, we report here the results for the naphthalene anion/alkali cation pair. The electrostatic interaction energy between naphthalene anion and a unit positive charge along lines of equidistance (1.5–2.0–2.5–3.0 Å) from the atoms of the anion in a σ , plane are reported in Fig. 2.

From these data and from analogous energy plots in a number of different planes, it appears that in the region nearer to the anion (distance range 1.5–1.8 Å) two equivalent minima are present, separated by a barrier 13 kcal/mol high. At distances larger than 2.0 Å only one flat minimum is present, located over the centre of the radical (Cremaschi *et*

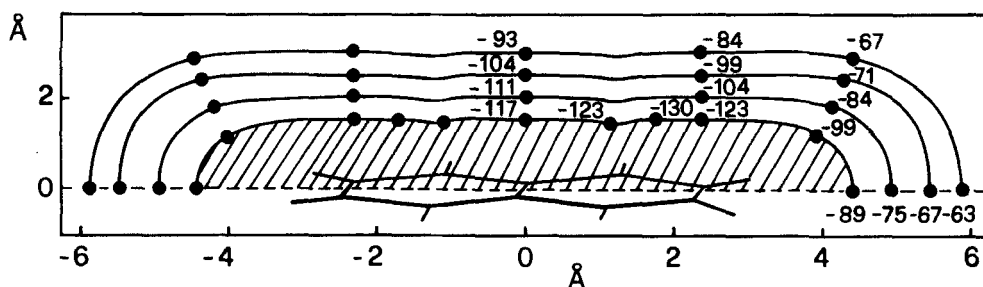


FIG. 2. Energy values along equidistance lines (1.5, 2.5 and 3 Å) in a σ , plane of naphthalene anion.

al., 1976b). So we may expect that a small cation can be found in one of the two symmetric wells over the centre of the rings. In order to preserve molecular symmetry in the spin distribution, the cation must jump rapidly from one minimum to the other. Indeed for Li^+ the metal hfs quartets exhibit linewidth variations that have been interpreted as due to motional modulations (Atherton, 1966; Williams *et al.*, 1970; Dodson and Reddoch, 1968).

More interesting situations are found with heterocyclic anions. When 4-nitropyridine is reduced with Li, Na or K in tetrahydrofuran or dimethoxyethane (Cremaschi *et al.*, 1975a), the corresponding ion pairs are formed. The ESR spectra show metal splitting, equivalence of the two ortho and meta hydrogen atoms and a positive gradient of hfs constants of all metals with increasing temperature. No evidence for the free anion was found, suggesting that the ion pairs are of the tight type.

Comparison of the splittings of the nitrogens of the free anion and of the ion pair shows a stronger perturbation on the nitrogen of the nitro-group, the temperature dependence of the metal splittings parallels that found in the nitrobenzene ion pair, while it is reversed in the pyrazine-sodium pair; a nice correlation exists between nitro-group nitrogen and metal splittings, but not between splittings of the metal and of the ring nitrogen. All these facts favour a strong interaction between the cation and the nitrogen of the nitro-group, inducing an electron transfer from the ring nitrogen towards the nitro-group. The electrostatic potential has been evaluated in the space surrounding the anion, based on an *ab initio* unrestricted wavefunction of the STO-3G type. The potential has not been evaluated in the region within 1.5 Å of the anion since electron-electron repulsion (not included in our model) would prevent the cation approaching the anion nearer than about the sum of the Van der Waals radii. The potential shows an absolute minimum along the symmetry axes in the region of the nitro-group. A secondary minimum is present in the region of the ring nitrogen, but the energy barrier between the minima is high enough to prevent cation jumps. In fact no linewidth variations within alkali multiplets were observed. In conclusion, the calculated potential provides a rationale for all experimental facts. A different situation was found when Cs or Rb metals were used for reduction with the same solvents (Gamba *et al.*, 1975). Here the metal hyperfine splitting is absent and the number of magnetic nuclei to obtain simulated spectra is twice the number of magnetic nuclei of the free anion. When dimethylsulphoxide is added to the solution the spectrum changes to that of the free anion. While various interpretations of these phenomena were offered, no geometrical model could be established to warrant quantum-mechanical calculations. In addition the difference between the Cs and Rb spectra suggests different packings of the fragments. The ESR spectra of 4-nitropyridine N-oxide with Li, Na, K, Rb and Cs were also studied (Gamba *et al.*, 1976). The electrostatic potentials in the anion molecular plane and in parallel planes 1.5 and 3.0 Å above it are shown in Fig. 3.

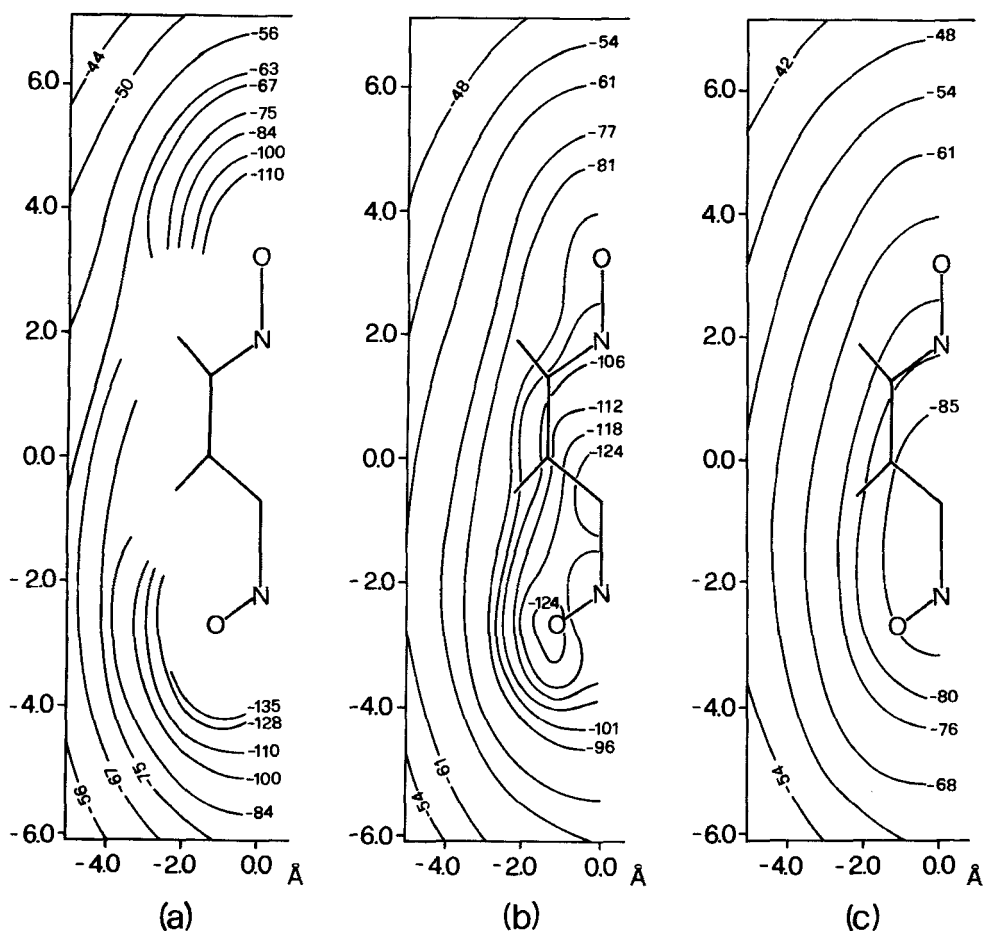


FIG. 3. Potential maps for 4-nitropyridine N-oxide (a) molecular plane; (b) 1.5 Å above; (c) 3.0 Å above.

The splitting of the alkali metal is present in all complexes from Li to Cs. The changes in the hfs constants of the nitrogen of the nitro-group parallel those of the aromatic nitro-derivatives, suggesting a localization of the cation in the region of the nitro-group. Two superimposed spectra are present in the case of Li and Na. The surfaces of Fig. 3 show that at 1.5 Å two relative minima are present besides the absolute minimum in the nitro-group region. The intermediate minimum is above the carbon that carries the substituent. This minimum disappears at 3 Å, and this behaviour could explain the existence of two ion pairs in the Li and Na complexes, and the presence of only one pair in the K complex. The most important features of the potential surfaces for pyrazine radical anion are shown in Fig. 4 (Cremaschi *et al.*, 1975b).

At 1.5 Å there are two equivalent absolute minima, separated by a barrier 25 kcal/mole high and one relative minimum, separated by a barrier of about 6 kcal/mole. At increasing distances first the relative minimum disappears and then, starting at 3 Å, only one minimum is present, located above the centre of the ring. These results are in nice agreement with experimental findings. For K, Rb and Cs ion pairs, the cation has been localized above the centre of the pyrazine radical anion. For Li and Na ion pairs, linewidth

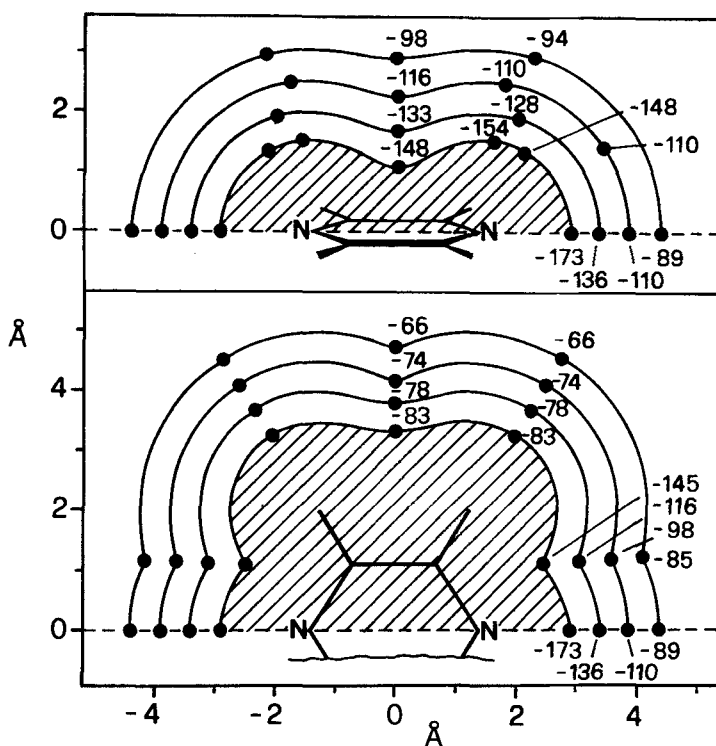


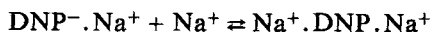
FIG. 4. Equidistance lines (1.5–2.0–2.5–3.0 Å) in the σ_v (above) and σ_h (below) plane of pyrazine radical anion, and electrostatic potential values.

alternation has been attributed to intramolecular cation exchange with estimated barriers of 13 kcal/mole for Li^+ and 7 kcal/mole for Na^+ .

Potential surfaces have also been obtained for ortho, meta and para dicyanobenzene radical anions (Cremaschi *et al.*, 1975). Two equivalent absolute minima are present in the molecular plane, at about 1.5 Å from the nitrogen atom. A relative minimum is also present in the plane 1.5 Å above the benzene ring. The barrier height between absolute and relative minima is about 30 kcal/mole for ortho and meta and 24 kcal/mole for para isomers. Starting from distances of 2 Å from the anion, only one minimum, above the benzene ring, is present in the case of meta and para isomers, while for the ortho isomer two equivalent minima are present, both in the σ_v plane, one in the molecular plane close to the cyano groups, the other above the benzene ring, separated by a barrier of 4–5 kcal/mole. From the analysis of the ESR spectra of ion pairs of ortho and para isomers and the lightest alkali cations, intramolecular cation transfer between equivalent positions has been established. The calculated potential surfaces show an activation barrier of 13 kcal/mole for the ortho isomer along a path in the molecular plane. For the para isomer a cation jump out of the molecular plane is possible, with a barrier of about 24 kcal/mole. No experimental data are available at present for the meta isomer, for which quantum-mechanical results suggest the formation of an asymmetric ion pair, at least with the lightest alkali cations.

Ion pairs formed by reduction of 3,5-dinitropyridine with alkali metals have been investigated in the same way (Barzaghi *et al.*, 1978). The electrostatic interaction energy

maps lead to the conclusion that two equivalent absolute minima exist in the molecular plane, in the region of the two nitro-groups. High energy barriers (>50 kcal/mole) separate the two minima, as well as a relative minimum in the region of the ring nitrogen. The experimental spectra confirm these results: the hfs constants of the nitro-group nitrogens are widely different and the metal splittings are easily visible, suggesting that the cation is located near one nitro-group to form a strongly associated ion pair. The lack of linewidth alternation due to dynamic processes and the absence of the free-ion spectra confirm this interpretation. When sodium tetraphenylborate is added to the sodium ion pairs solution, however, a sodium exchange reaction occurs, with formation of a triple ion. From ESR line-shape and temperature-dependence analysis, a simple theoretical model for intermolecular cation transfer has been found and both the equilibrium and ionization rate constants for the reaction



were obtained. The dependence of the observed rate of line-broadening processes on salt concentration confirms that the cation exchange is intermolecular and linewidth analysis

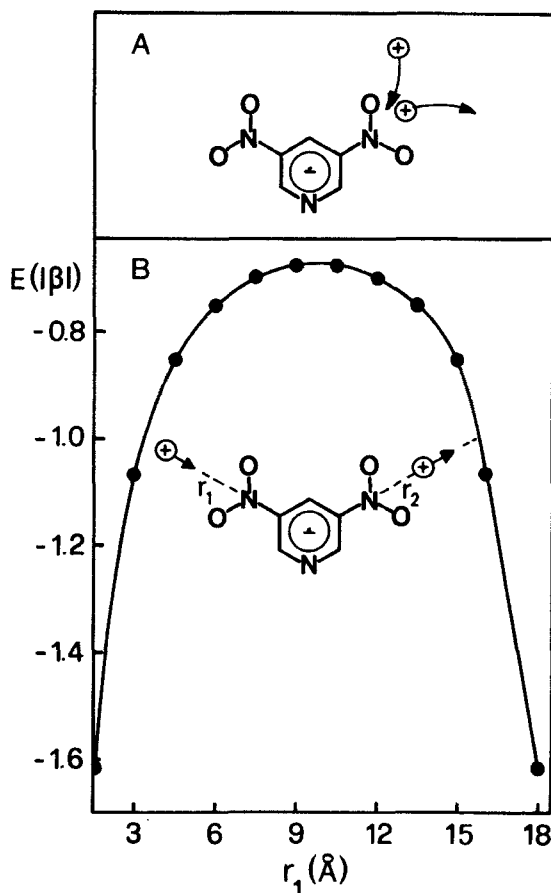


FIG. 5. Possible reaction mechanisms for cation exchange in 3,5-dinitropyridine and energy barrier for mechanism B.

favours mechanism *B* with respect to *A*, shown in Fig. 5, where the energy variation along *B* has been calculated according to the McClelland (1961) procedure.

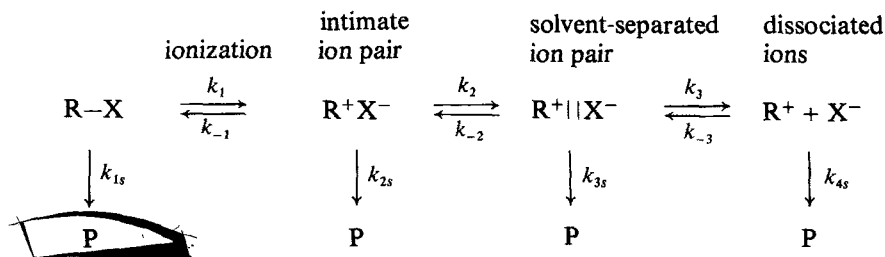
An analogous behaviour was found for 3,5-dinitrobenzotrile sodium in tetrahydrofuran containing sodium tetraphenylborate (Barzaghi *et al.*, 1980). Again the analysis of ESR spectra has shown that in the absence of the salt a strongly associated ion pair is formed when the cation is localized near one nitro-group. When NaBPh₄ is added, significant changes in the ESR spectra are observed due to the formation of triple ions which can be present as intermediates in the intermolecular cation transfer between the two equivalent nitro-groups at which ionic association can occur. Potential energy maps have not been calculated for this special case, since they are expected to be very similar to those for 3,5-dinitropyridine.

For all the systems mentioned the hfs constants of magnetic nuclei have been obtained from the spectra, and calculated by means of the McLachlan (1960) method, as modified by McClelland (1961), with reasonably good fit. This topic is not considered in the present review, though the values of the hfs constants are helpful in confirming our models.

In all studies presented in this review, the molecular potential approach at the electrostatic approximation level can be recognized as a significant important tool to be used in connection with experimental results for the structure determination of ion pairs in solution. However, there are situations in which this approximation breaks down. An example is found in the case of the lithium-allyl ion pair, where the barrier to rotation of one methylene group has been found to be 10.7 kcal/mole high (Thompson *et al.*, 1979). Here the potential maps suggest the existence of two minima at the 1.5 Å distance, right above the end carbon atoms (Cremaschi *et al.*, 1980). On the contrary, molecular orbital calculations for the C₃H₅Li system (Bengini *et al.*, 1976; Clark *et al.*, 1978) show that only one minimum is present, with Li⁺ located in the region of the central carbon. The empty *p* orbital of Li allows a strong interaction with the non-bonded orbital of the allyl fragment with consequent stabilization of this geometry due to considerable charge transfer. The danger of overlooking this and polarization effects decreases sharply with increasing anion-cation distance.

DIAMAGNETIC ION PAIRS

After differentiation between dissociated carbonium ions and carbonium ion pairs, two kinds of ion pairs were recognized in Winstein's (1965) work, namely an intimate ion pair with the two ions in the same solvent cage, and a solvent-separated ion pair, with the two ions in separate, but adjacent, solvent cages. Accordingly, the following scheme can be formulated for the solvolytic reaction of an alkyl halide



While this scheme has been suggested after a vast amount of experimental work, no information had been produced to elucidate the structure of the two kinds of ion pairs, neither theoretically nor experimentally, until recently when a molecular orbital study for

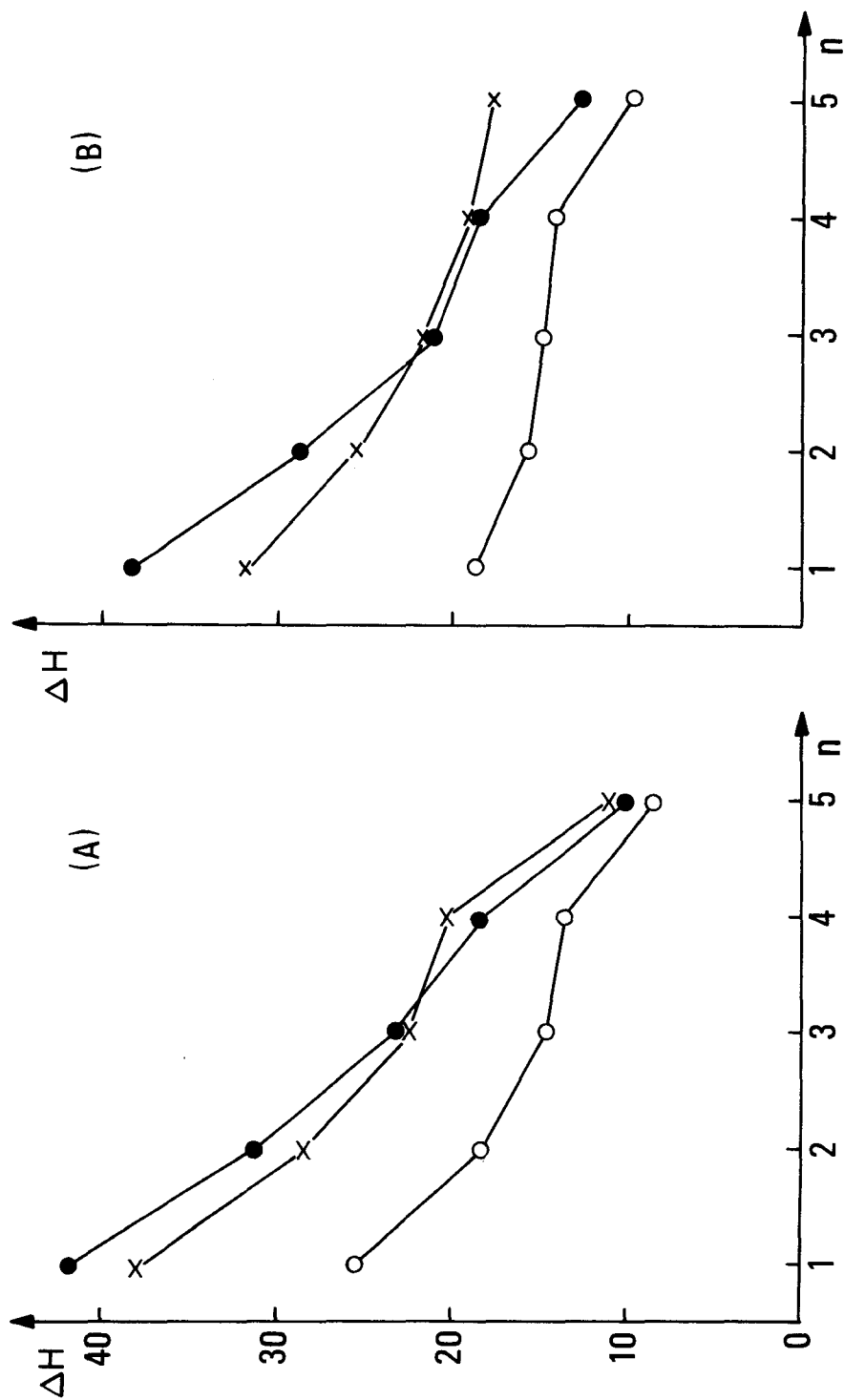


FIG. 6. $\Delta H_{n,n-1}$ (kcal/mole) for successive additions of ligands to NH_4^+ . (A) for $(\text{NH}_4.n\text{NH}_3)^+$, (B) for $(\text{NH}_4.n\text{H}_2\text{O})^+$. (O) exp; (X) CNDO; (●) *ab initio*.

dissociation of CH_3F in water was produced (Cremaschi *et al.*, 1977). The choice of this particular system is chiefly due to its small size: the solvent cage can be built with a reasonable number of water molecules. In fact we studied the supermolecule $\text{CH}_3\text{F} \cdot 11\text{H}_2\text{O}$. The number of water molecules is obtained as the sum of the water molecules needed for solvation of the F^- (6) and CH_3^+ (5) ions. The same number was suggested on thermodynamic grounds (Glew and Moelwyn-Hughes 1953).

The standard CNDO/2 method (Pople and Beveridge, 1970) was chosen since it had been satisfactorily used to study the influence of solvation on the activation energy for the reaction $\text{CH}_3\text{F} + \text{F}^-$ in water (Cremaschi *et al.*, 1972), the shifts of $n-\pi^*$ and $\pi-\pi^*$ transition energies in UV spectra of conjugated systems on going from polar to non-polar solvents (Cremaschi *et al.*, 1973), the relative stability of different conformations of the CH_3^+ ion in solution (Cremaschi and Simonetta, 1975a), and the influence of solvation on the rotational barrier in CH_3-NH_3 (Cremaschi and Simonetta, 1975b). An interesting example of the reliability of this particular approximation is the calculation of the solvation energy of the ammonium ion with H_2O or NH_3 , for which accurate experimental data are available (Payzant *et al.*, 1973). In Fig. 6 CNDO results are compared with experiment and *ab initio* results (Pullman and Armbruster, 1975).

The energy of the supermolecule $\text{CH}_3\text{F} \cdot 11\text{H}_2\text{O}$ has been calculated at different C-F distances from 1 to 10 Å keeping the C-H bond lengths at the constant value 1.12 Å, and assuming the three HCH angles always to be equal.

The 11 water molecules were kept rigid with the geometry calculated for the isolated molecule, and partial local symmetries were retained in order to reduce the variables to a reasonable number.

The results are shown in Fig. 7, where three minima are clearly localized. The first minimum at C-F = 1.39 Å corresponds to the covalent R-X molecule in solution. Due to solvation the C-F bond length is slightly increased from the 1.34 Å value calculated for the isolated molecule (Cremaschi *et al.*, 1972) and the negative charge on F is increased from 0.185 to 0.255 (in electron units). The water molecules build a cage surrounding the solute molecule. The second minimum is found at 3.48 Å. Now the charge on F is 0.52 and two water molecules sit close to the C-F bond, each one with an O-H bond almost parallel to the C-F direction, the hydrogen atom being on the fluorine side. With further extension of the C-F bond, two water molecules enter into the region between C and F and the third minimum is found at $r = 5.46$ Å. The two ions are now in two different but adjacent solvent cages. The charge on F is 0.53 to be compared with the value found in

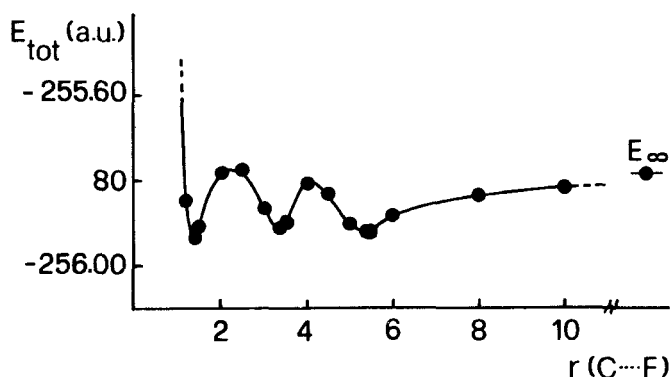
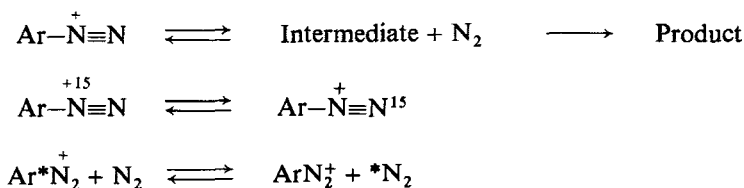


FIG. 7. Energy of $\text{CH}_3\text{F} \cdot 11\text{H}_2\text{O}$ at different C-F distances.

($F \cdot 6H_2O$)⁻, 0.56. Further increase of the C—F distance is paralleled by an increase in energy, since we are now separating two charged species, and working against Coulomb attraction. These results must be considered with caution. Entropy effects have been ignored though many configurations of almost equal energy actually exist: and the interaction between the first solvation shell and the bulk of the solvent can influence their relative stability. Furthermore water should be allowed to react and at least one O—H distance should be relaxed. However, these results show unequivocally that the presence of a shell of polar molecules can stabilize ion pairs of different kinds, and a qualitative representation of the mechanism by which CH_3F molecules dissociate in water is offered.

A similar case can be found in the work of Zollinger *et al.* on the mechanism of dediazonium reactions (Szele and Zollinger, 1978; Hashida *et al.*, 1978). Here kinetic evidence has been presented for the formation of intermediates during the reaction, showing that a rearrangement and an exchange reaction compete with the decomposition, according to the following scheme:



This time the intermediate is an ion-molecule pair. Again CNDO/2 calculations have been performed for the dissociation of a model cation, namely benzenediazonium, in a model solvent, water (Gamba *et al.*, 1980a). It has been found that only a limited number of water molecules, six or seven, are needed to surround the carbon atom to which the leaving

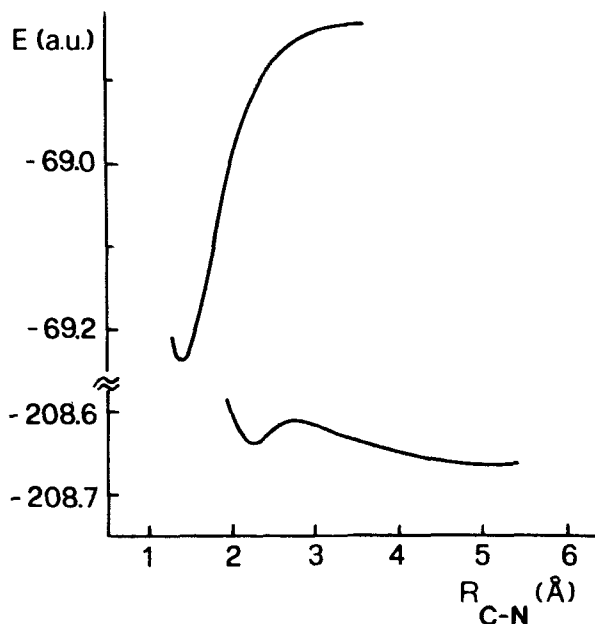


FIG. 8. Dissociation energy of $C_6H_5N_2^+$ in the gas phase (upper curve) and in solution (lower curve).

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