ASSOCIATION OF RADICAL ANIONS WITH ALKALI METAL CATIONS; I. MODIFIED π(PPP-LIKE) METHOD FOR THE INVESTIGATION OF ION PAIRS

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A simple π-approximation (PPP-like) method was modified to enable study of the association of radical anions with alkali metals. The possible uses of the method are demonstrated by the calculations of the different properties of the pyrazine–Me (Me = Li, Na, Cs) system.

In recent years, considerable attention has been devoted to experimental and theoretical studies of the formation of radical anions and their associates with alkali metal cations[1–3]. From the theoretical point of view, interest has centred on calculation of the electronic structures of ion pairs, interaction energies, the most stable position of a cation with respect to the radical anion and hyperfine splitting constants. From the viewpoint of exactness, methods used for calculating ion pairs can be divided into:

a) empirical[4–6], *b*) semiempirical[7,8] and *c*) non-empirical[9–11]. Among the empirical methods, a simple HMO method was employed, including electrostatic interaction of radical anions with a cation as a point charge. In the second group[7,8], the EHT and CNDO methods were applied to the supersystem radical anion + cation. As long as the individual parameters were not modified compared to the original ones, contradictory results were obtained. Using *ab initio* calculations, a radical anion + + cation was either considered as a supersystem[9,10] or the effect of the cation was expressed in terms of the electrostatic potential of a point charge[11]. In the first case, wrong results for hyperfine splitting constants were obtained and in the second reliable information of the interaction energy between a cation and a radical anion could not be obtained. As shown previously[7,8,11], the solvent effect on these systems is considerable and has to be taken into account in the calculation. A shortcoming of the *ab initio* methods is their great consumption of computing time and memory, because the majority of the experimentally studied systems concerns large conjugated molecules.

In the present paper, an attempt was made to develop a simple method which would give reasonable results in calculating the interaction energy, the most stable configuration of cations with respect to radical anions, the charge or unpaired electron distribution and solvent effect on this system. For this purpose, the restricted LHP method[12] in the π-approximation (PPP-like) was modified. Possibilities of the method were tested on several different systems of radical anions and cations.

Methods and Calculations

We included the valence s-orbital of the alkali metal formally in the π system. It is necessary to find the respective parameters for such an orbital, namely the valence s-state ionization potential I_{Me}, the monocentric repulsion integral γ_{MeMe}, and the resonance integral $\beta_{\mu Me}$. The parameters I_{Me} and γ_{MeMe} can be obtained from the experimental values of the atomic spectra[13] or by taking the parameters from the CNDO method. For example, for the Li 2s orbital, $I_{Li} = 5{\cdot}39$ eV and $\gamma_{LiLi} = 6{\cdot}44$eV. The use of such parameters in the calculation by the π method does not, however, yield good results. For instance, the unpaired electron in the pyrazine–Li system is localized predominantly on Li, ref.[14]. This is partly due to the use of parameters inconsistent with the semiempirical parameters employed in the π method. In addition, solvation of the cation supports electron transfer from the neutral alkali metal to the π system and therefore this process can in principle be, described by including the solvent effect on the parameters of the alkali metal.

The qualitative effect of solvation can be estimated according to the method depicted in our recent paper dealing with the solvent effect on radical anions[15]. For the solvated alkali metal there is a diagonal matrix element

$$F_{Me} = F^{0}_{Me} - k_{\varepsilon} Q'_{Me} \gamma_{MeMe} - k_{\varepsilon} \sum_{v \neq Me}^{N} Q'_{v} \gamma_{vMe} \,, \qquad (1)$$

where F^{0}_{Me} is the matrix element without considering solvation, the solvent constant $k_{\varepsilon} = 1/2(1 - 1/\varepsilon)$ and ε is the dielectric constant.

As the net solvation charge, Q'_{Me}, near the cation is negative and close to $-1{\cdot}0$ and its absolute value is much greater than charges Q'_{v} near the radical anion atoms, it will hold that

$$F_{Me} > F^{0}_{Me} \,. \qquad (2)$$

As matrix element F_{Me} is

$$F_{Me} = -I_{Me} + 1/2 P_{MeMe} \gamma_{MeMe} + \sum_{v \neq Me}^{N} (P_{vv} - Z_{v}) \gamma_{vMe} \qquad (3)$$

qualitative the same effect can be achieved by decreasing the I_{Me} value or by increasing γ_{MeMe}. Therefore, we modified the parameters of the alkali metals in the appropriate way, the calculation of the solvation energy being carried out according to the relationship[16]:

$$-E_{\text{solv}} = 1/2 \sum_{\mu,\nu} Q_\mu Q_\nu \gamma_{\mu\nu}(1 - 1/\varepsilon)\,. \tag{4}$$

The results of this modified calculation of the pyrazine–Li system were in qualitative agreement with the experimental data. For I_{Me} for for Li and Na cations the values $1/2(I_{\text{Me}} + A_{\text{Me}})$ from the CNDO/2 method were used. For Cs the I_{Me} value was extrapolated (Table I). To determine γ_{MeMe} the relation (4) for the solvation energy was used, according to which for the alkali metal cation

$$-E_{\text{solv}} = 1/2(1 - 1/\varepsilon)\,\gamma_{\text{MeMe}}\,. \tag{5}$$

Hence for γ_{MeMe}

$$\gamma_{\text{MeMe}} = -2E_{\text{solv}}(1 - 1/\varepsilon)\,. \tag{6}$$

If for E_{solv} are used the experimental solvation energies of alkali metal ions in water[17], the γ_{MeMe} values obtained (Table I) are higher than those determined from the expression $(I_{\text{Me}} - A_{\text{Me}})$. It was also found that use of the γ_{MeMe} values obtained in this way improves the results of the calculation of the structure of the pyrazine–Li ion pair.

In our method, the resonance integrals for non-neighbouring atoms were considered according to the relationship[18]:

$$\beta_{\mu\nu} = C\,\frac{2I_\mu I_\nu S_{\mu\nu}}{I_\mu + I_\nu}\,. \tag{7}$$

TABLE I

Monocentric Integrals for LHP-π Calculations

Atom	I_μ, eV	$\gamma_{\mu\mu}$, eV
C	11·16	11·13
N	14·12	12·34
O	17·70	15·23
Li	3·10	10·30
Na	2·80	8·40
Cs	2·35	5·12

The overlap, $S_{\mu\nu}$, for the C, N and O atoms was calculated from the p_z Slater atomic orbitals and the constant $C = 0{\cdot}52$. To express the resonance integrals between an alkali metal and atoms forming the π-system, the same relationship (7) was used with the constant $C = 0{\cdot}208$; however, the overlap was calculated from the respective valence s-functions (at both the metal atom and the atoms of the π-system) so that it does not depend on the spatial orientation of the metal to the π-system.

For I_μ and $\gamma_{\mu\mu}$ of the other O, C and N atoms the standard parameters according to Hinze and Jaffé were used[19] (Table I).

The total energy of the system E_T in the LHP–π method is usually expressed as follows

$$E_T = E_{\pi el} + E_{rep}\,, \qquad (8)$$

where $E_{\pi el}$ is the electronic energy of the system and E_{rep} stands for the energy of the "core–core" repulsion

$$E_{rep} = \sum_{\mu<\nu}^{N} Z_\mu Z_\nu \gamma_{\mu\nu}\,. \qquad (9)$$

The total energy of the pyrazine–Li system calculated according to the above relationships when Li approaches pyrazine, decreases and reaches minimum only at very small distances which are physically unjustifiable. This fact, similar to the effect known in the literature as a "molecular collapse" is due to the lower value of the repulsion energy.

To compensate the attraction and repulsion forces we used a modified expression for the repulsion (between the "core"–Li and "core" atoms of pyrazine) according to Dewar and Haselbach[20]

$$E_{rep} = Z_\mu Z_{Me}\gamma_{\mu Me} + (14{\cdot}3986 Z_\mu Z_{Me}/r_{\mu Me} - Z_\mu Z_{Me}\gamma_{\mu Me})\exp\left(-\alpha_{\mu Me} r_{\mu Me}\right), \qquad (10)$$

where $r_{\mu Me}$ is the distance between Li and the centre of the atom; $\alpha_{\mu Me}$ are the empirical parameters for alkali metals.

The α parameters were chosen so that the energy minima of the pyrazine–Li system correspond to *ab initio* calculations[9].

Then the following values were obtained:

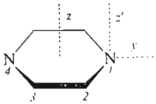
$$\alpha_{NLi} = 13{\cdot}0\ \text{nm}^{-1}\,,$$

$$\alpha_{CLi} = 7{\cdot}0\ \text{nm}^{-1}\,.$$

The α_{OLi} parameter was found so that the minimum of the total energy of the *cis*-glyoxal–Li system would be between 0·2–0·3 nm. Such a result was obtained using the parameter $\alpha_{OLi} = 10{\cdot}0\ \text{nm}^{-1}$. The α values of the parameters were used for all other systems.

RESULTS AND DISCUSSION

The method developed was used for studying several radical anion + cation systems. A more detailed analysis of calculations will be carried out for the pyrazine–Me system (where Me = Li, Na, Cs) belonging to the most frequently investigated radical anion–cation associates: The approach of Li to pyrazine in three directions, *Y*, *Z'*, and *Z* (see structure *I*) leads to charge transfer from the alkali metal to pyrazine. This transfer for Li is greatest in the *Y* direction. Fig. 1 shows the slope of the dependence $(1 - q_{\mathrm{Li}})$ as a function of the distance r_{Li}. Similar dependences will be obtained for Na, the greatest amount of the transfer (0·99 e) being in the *Y* direction. At the same time, exchange of the singly occupied MO and the first unoccupied MO occurs. For distances r_{Li} greater than 0·4 nm in each of the three directions, the singly occupied MO is localized mainly on the Li and the first unoccupied MO on the π-system of pyrazine. As Li approaches pyrazine, the MO energy change takes place: the singly occupied MO is the orbital localized predominantly on the π-system of pyrazine (with small admixture on Li).



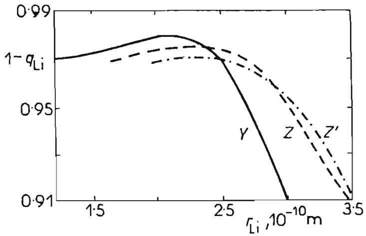


FIG. 1

Dependence of Charge Transfer from Li to Pyrazine on Distance r_{Li} in Directions *Y*, *Z*, *Z'* (see structure *I*)

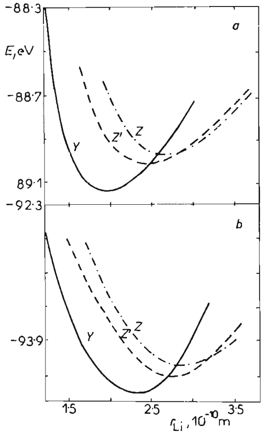


FIG. 2

Dependence of the Total Energy *a* E_{T}, for the Pyrazine Li System on Distance r_{Li} in Directions *Y*, *Z*, *Z'*; *b* E'_{T}, (including the solvation energy) for the pyrazine Li System on r_{Li} in Directions *Y*, *Z*, *Z'*

Simultaneously, we computed the dependences of the total energy E_T, with minima in all three directions; in the Y direction Li is localized 0·2 nm from nitrogen atom, in the Z' direction 0·24 nm from nitrogen atom and in the Z direction 0·26 nm from the centre of the ring (Table II). The most stable localization is in the Y direction (Fig. 2*a*). When using the same α parameters for sodium, its most stable positions were obtained in each of the three directions but at greater distances than for Li ($Y = 0·215$; $Z' = 0·26$; $Z = 0·28$ nm).

Our calculations for Cs using the unchanged α_{Me} parameters, however, also give the most stable position in the Y direction. The localization is 0·09 eV more stable than that in the Z direction.

Consideration of the sum of the total energy and solvation energy computed according to relationship (*4*) yields new variations of the energy with distance r_{Me}. Fig. 2*b* shows these dependences for the pyrazine–Li system for $\varepsilon \to \infty$. Incorporation of the solvent energy results in a shift of the minimum in the Y direction from 0·2 to 0·23 nm, in the Z' direction to 0·26 nm and in the Z direction to 0·29 nm. This is brought about by the fact that part of the solvation energy expressed as $-1/2(1 - 1/\varepsilon) \sum_{i \neq Me} Q_i Q_{Me} \gamma_{iMe}$ is positive and decreases with increasing distance r_{Me}, whereas the rest of the solvation energy is, in principle, independent of r_{Me}. Solva-

TABLE II

Energy Minima, Most Stable Distance of Alkali Metals in Ion Pairs of Pyrazine

Direction	$-E_{min}$ eV	r_{min} 10^{-1} nm	$-(E + E_{sol})_{min}$ eV	r_{min} 10^{-1} nm
		Li		
Y	89·1502	2·0	94·5211	2·3
Z'	89·0173	2·4	94·3146	2·7
Z	88·9707	2·6	94·1798	2·8
		Na		
Y	88·9907	2·15	93·8006	2·6
Z'	88·8869	2·6	93·4297	2·8
Z	88·8581	2·8	93·3597	3·0
		Cs		
Y	85·9522	2·3	89·5232	2·95
Z	85·8633	3·05	89·1347	3·2

tion exerts a stabilization effect on ion pair, especially in the Y direction, as the charge transfer from Li to pyrazine is greatest here and the solvation energy is largest. The difference between the minimum in the Y and Z' directions is 0·206 eV here (20 kJ . . mol^{-1}) and for the Y and Z directions 0·314 eV (30 kJ mol^{-1}). Similar changes caused by solvation also take place with the pyrazine–Na ion pair.

Another problem concerns the energy ratios of the free ions, ion pairs and neutral substances, both for the non-solvated system and for the system in a completely solvating solvent. Fig. 3 shows these energy changes in the pyrazine–Li system *in vacuo* ($\varepsilon = 1$) and in a completely solvating solvent ($\varepsilon \to \infty$). Here the most stable ion pair is that with an absolute energy minimum at a distance of $r_{\mathrm{Li}} = 0{\cdot}2$ nm. The solvent effect leads to stabilization of the individual systems, the free ions being stabilized most, the ion pair less and the neutral substances least. It follows from Fig. 3 that in the solvating medium the free ions are 0·59 eV (57·3 kJ mol^{-1}) more stable than ion pairs. For Na the situation is similar, where the solvated free ions are 0·3 eV (29 kJ mol^{-1}) more stable compared with the ion pairs in a completely solvating medium.

The energy difference between neutral substances and ion pairs which is too great for the pyrazine–Li system 6·5 eV (630 kJ mol^{-1}) does not correspond to the experimental energy effects in the formation of ion pairs found for other systems (40 – 80 kJ mol^{-1})[21].

Because the solvation energy expressed according to Eq. (*4*) increases for free ions with increasing ε more rapidly than for the ion pair, there is an ε' value for which energy $E_{\mathrm{T}} + E_{\mathrm{solv}}$ of the ion pair is the same as that of the free ions. If the solvation energy of the ion pair depends on ε according to relation $E_{\mathrm{solv}}^{\varepsilon} = E_{\mathrm{solv}}^{\varepsilon\to\infty}(1 - \varepsilon^{-1})$, it holds that

$$E_{\mathrm{T}}^{\mathrm{ip}} + E_{\mathrm{solv}}^{\varepsilon\to\infty}(1 - \varepsilon^{-1}) = E_{\mathrm{T}}^{\mathrm{ar}} + (E_{\mathrm{solv}}^{\mathrm{ar}} + E_{\mathrm{solv}}^{\mathrm{Me}^+})(1 - \varepsilon^{-1}) . \qquad (11)$$

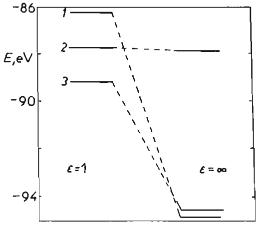


FIG. 3

Variation of the Total Energies of Various Forms of the Pyrazine Li System Accompanied by a Change of the Value of ε from 1 to ∞

1 Free ions; *2* Neutral species; *3* Ion pair.

Solving this equation yields $\varepsilon' = 5{\cdot}9$ for Li, and $\varepsilon' = 8{\cdot}4$ for Na. These results can be qualitatively interpreted so that in medium polar solvents (dimethoxymethane, diethylether) ions pairs are preferred more than in strongly polar solvents (acetonitrile, hexamethylfosforamide), where free ions should predominate. The experimental findings do not contradict this assumption as the ion pairs were prepared in moderately polar solvents ($\varepsilon = 4-10$).

Determination of the structure of the ion pair according to the minimum of the total energy (including the solvation energy) is of considerable importance for further evaluation of the cation effect on the radical anion in an ion pair. The energy differences between the individual minima for the given system have also reasonable values. In pyrazine, migration of the cation from one nitrogen to another was found experimentally[22]. The activation energy for this process for Na is 30 ± 2 kJ mol^{-1}. On the basis of the calculation described in this paper, it can be assumed that the reaction path for such a migration leads from the energy minimum in the Y direction (near one nitrogen) through the minima in the Z' and Z directions; the minimum in the Z direction represents the highest point of the reaction pathway (activated complex) and the energy difference ($E^{Z}_{\mathrm{min}} - E^{Y}_{\mathrm{min}}$) incorporating solvation represents the activation energy. In our calculation this is 42 kJ mol^{-1}, which, considering the simplicity of the model, is a reasonable value.

Interpretation of ESR *Spectra for Ion Pairs*

The change of the electronic structure in the radical anion itself resulting from the formation of ion pairs will be manifested in a change in the ESR spectra, mainly in a change in the hyperfine splitting constants. From the experimental point of view, observation of the changes in ESR spectra is one of the most advantageous methods for studying the formation of ion pairs or other associates and their mutual equilibrium.

Changes in ESR spectra are observed in two respects: *a*) observation of the hyperfine splitting constants for various spin active nuclei of radical anion atoms (^{13}C, ^{14}N, ^{1}H;) *b*) observation of the formation of splitting for the alkali metal in ion pair formation. These changes can be studied by the method worked out in the present paper. Spin densities were calculated according to relationship[23] where the total value of the spin density results both from the wave function of the ground state and also from the spin polarized wave function, $^{2}\psi_{\mathrm{C}\beta}$. This procedure is common for calculation of the spin densities on the radical anion. The problem of the existence of spin density on an alkali metal cation seems to be more complicated than it actually is. In addition to transfer of an unpaired electron from the radical anion to the cation, a contribution from local excitation (*i.e.* polarization of electrons from the inner shells to the valence ones) is possible[24].

However, in a detailed analysis, Canters and coworkers[25] have shown that this contribution is, as a rule, much smaller than delocalization of unpaired electron to the cation or smaller than the contribution from the ${}^2\psi_{C\beta}$ function describing excitation from the doubly occupied MO to the unoccupied MO located on the cation.

The calculated spin densities were converted to the hyperfine splitting constants according to relations taken from the literature. For the a_H constants, the Colpa–Bolton relation was used

$$a_H^i = (Q_1 + Kq_i^c)\,\varrho_i\,, \tag{12}$$

q_i^c being the net charge on atom i and $Q_1 = -2{\cdot}7$ mT and $K = 1{\cdot}82$ mT, ref.[26]; for a_N

$$a_N^i = Q_N\varrho_i - Q_{CN}(\varrho_j + \varrho_{j'})\,, \tag{13}$$

where ϱ_j, $\varrho_{j'}$ are the spin densities on carbon atoms adjacent to nitrogen atoms. The values of the Q_N and Q_{CN} constants are taken from[27] $Q_N = 2{\cdot}2$ mT and $Q_{CN} = -0{\cdot}2$ mT.

Conversion of the spin density, ϱ_{Me}, was carried out according to Goldberg and Bolton[6] who used the simple McConnell relation

$$a_{Me} = Q_{Me}\varrho_{Me}\,, \tag{14}$$

where Q_{Me} is the constant obtained from the ESR spectra of vapours of alkali metals and equals 14·3 mT.

For the pyrazine–Li system, all hydrogen and nitrogen atoms are equivalent only if Li^+ lies in the Z direction. On the contrary, if Li^+ lies in the Y and Z' directions, different splitting constants are obtained for protons and for nitrogen atoms. Dependences of the proton hyperfine splitting constants on the distance of the Li cation in individual directions and nitrogen splitting constants for the Y direction plotted as a function of r_{Li} are depicted in Fig. 4*a*,*b*. The values for the free radical anion are plotted for $r \to \infty$, *i.e.* the most stable position of Li in the solvated ion pair.

The different values of the splitting constants for nitrogen atoms as well as for protons were found experimentally[22]. This eliminates the possibility of location of the cation in the Z direction, which is in agreement with the energies calculated in this paper for the individual directions. Moreover, the constants computed for the ion pair at the energy minimum (Y direction) including the solvation energy (0·23 nm) agree well with the experimental data[28] (Table III).

When Li^+ is replaced by Na^+, it was found experimentally[28] that nitrogen constants increase and, on a whole, the differences between them decrease. Proton splitting constants show the same trend. This is characterized by the calculation, as shown in Table III, listing the splitting constants calculated corresponding to the most stable localization in a completely solvating medium for Li and Na together with the experimental values. For the pyrazine radical anion the following values were obtained by the method employed: $a_N = 0{\cdot}715$ mT, $a_H = 0{\cdot}214$ mT. Fig. 5 depicts the calculated dependence of the hyperfine splitting constants at the alkali metal as a function of distance r_{Li}. At smaller distances the constants first have small positive and then small negative values but they rapidly increase at greater

TABLE III

Spin Densities and Hyperfine Splitting Constants for the Ion Pair Pyrazine $^{\overline{\cdot}}$ Me^+ (in 10^{-4} Tesla)

Parameter	Li_{exp}	Li_{calc}	Na_{exp}	Na_{calc}
ϱ_{N1}	—	0·319	—	0·33
a_{N1}	6·62	6·400	6·96	6·76
ϱ_{N4}	—	0·328	—	0·331
a_{N4}	7·28	7·050	7·32	7·10
$\varrho^{\pi}_{C2,6}$	—	0·133	—	0·125
$a_{H2,6}$	3·31	3·470	2·97	3·36
$\varrho^{\pi}_{C3,5}$	—	0·041	—	0·047
$a_{H3,5}$	1·94	1·13	2·27	1·36

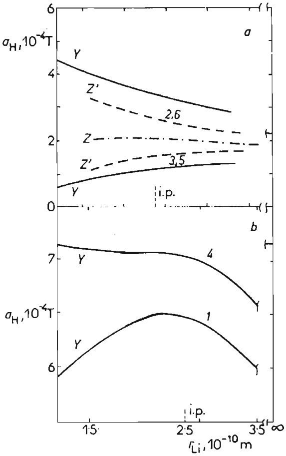


FIG. 4

Dependence of the Calculated Hyperfine Splitting Constants for the Pyrazine Li System on r_{Li} in Directions Y, Z, Z'

a Dependence a_H, *b* dependence a_N. Numbers denote atomic positions on pyrazine (see structure *I*) i.p. (ion pair) corresponds to the value of r_{Li} for the energy minimum of the system; $r_{Li} = \infty$ corresponds to the free radical anion.

distances. The negative values are a result of relatively significant contributions from the spin polarized wave functions $\psi_{C\beta}$. This contribution decreases by removing Li, the unpaired electron being transferred to Li.

By this calculation connected with LCI, the electronic transitions in the ion pair and free radical anion respectively were obtained. These, however, are not given here, as for pyrazine no comparable experimental results are available.

Concluding Remarks

Application of the π method to the nonplanar system and approximation of an atom containing an s electron and no p electron by the "p_z" orbital seems to be questionable at first sight. We do realize that this model is very approximate and has several shortcomings: *e.g.* with regard to the different symmetry of the s orbital of the alkali metal and of $2p_z$ orbital of the π system, calculated quasi π orbitals and the supersystem cannot be characterized by the natural symmetry of the system. Some effects (*e.g.* interaction of a cation with free electron pairs at heteroatoms of the π-system) are not included explicitly in the method. This method can be useful especially in applications to systems where a considerable part of electron is transferred from the alkali metal to the π-system. The proposed method characterized a number of properties of several different radical anion–cation systems surprisingly well, indicating wider validity of the parameters found for alkali metals. The method of treating the radical anion–cation system as a "supersystem" has some advantages compared with the purely electrostatic model as, among other things, it also provides information on the electronic structure of the alkali metal cation, where, under certain conditions, the spin density is observed. Expression of the solvation energy according to relation (*4*) represent one of the simplest models. It seems, however, that this model is sufficient because it adequately describes the electrostatic contribution to solvation

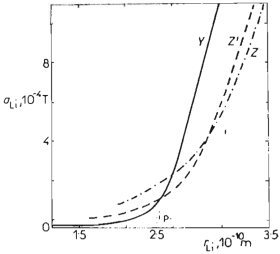


FIG. 5

Dependence of the Calculated Hyperfine Splitting Constant, a_{Li}, on r_{Li} in Directions Y, Z, Z'

energy which is dominant in the charged systems. Thus qualitative information can be obtained about the solvent effect on the structure of ion pairs. Further applications of the method to investigation of the structure of radical anion–cation associates and to a study of the reactivity in anionic polymerization will be considered in subsequent papers.

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