

carried out giving some theoretical background on the basis of quantum chemistry for this fundamental process of solution chemistry.

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Solute-Solute Interactions by NMR of Molecules Dissolved in Liquid Crystal Solvents: Pyridine – Iodine Molecular Complex in Nematic Phase

PIER LUIGI BARILI, CARLO ALBERTO VERACINI*

Istituti di Chimica-Fisica e di Chimica Organica dell'Università di Pisa, Via Risorgimento 35, 56100 Pisa, Italy

and MARCELLO LONGERI

Dipartimento di Chimica, Università della Calabria, Cosenze, Italy

NMR spectra of pyridine [^{14}N] and pyridine [^{15}N] partially oriented in nematic phase IV in presence of iodine show an increasing width as a function of the I_2 concentration. The observed spectral changes can be interpreted assuming that, as the molecular complex between iodine and pyridine is formed, a considerable variation in the orientation of pyridine moiety is produced.

Spectral analysis, performed by means of LEQUOR programme, reveals that the direct dipolar couplings (D_{ij}) are linearly dependent on the iodine concentration.

Our attempts to interpret the measured couplings on the basis of an average geometry and orientation of pyridine were unsuccessful leading to dramatic distortion effects on the apparent geometry. These results suggest that a two sites exchange mechanism is operating in the nematic phase, the two sites being the free pyridine and the complexed one.

By taking account of this exchange and using ^{15}N enriched pyridine an attempt was made to obtain the geometry and orientation of the pyridine- I_2 molecular complex.

Nuclear Quadrupole Coupling Constants of Small Ions in Aqueous Solution

SVEN ENGSTRÖM, BO JÖNSSON and HÅKAN WENNERSTRÖM

Division of Physical Chemistry 2, P.O.B. 740, S-220 07 Lund 7, Sweden

An atomic nucleus with a spin quantum number $I > \frac{1}{2}$ possesses a nuclear quadrupole moment, which, when interacting with an external electric field gradient, gives the so-called quadrupole coupling. This coupling plays a dominating role for the relaxation rates of NMR signals of quadrupolar ions [1], but it can also give additional splittings of signals in systems, where the field gradient does not average to zero at the nuclear site.

However, for a dilute aqueous solution of ions, the field gradient is caused by the surrounding water molecules, which, due to their motion, will average it to zero. Hence, there is no splitting, but the fluctuation of the field gradient will contribute to the relaxation. From the NMR experiment it is possible to estimate the product between the field gradient fluctuation, $\langle V_{zz}^2 \rangle_{\text{eq}}$, and a correlation time τ_c , associated with the motion of the water molecules.

In this work we have focused our interest on the field gradient at the ion nuclear site, and the origin of it. Therefore, calculations with the Monte Carlo simulation technique have been performed on systems consisting of 50 water molecules surrounding an ion (Li^+ , Na^+ and Cl^-). The configurations generated in the simulation have been used to calculate the field gradient fluctuation at the nuclear site of the ion. The results have been compared with experimental and other theoretical data.

The analytical expressions for the intermolecular pair-potentials used in the Monte Carlo program, have been obtained from fittings of accurately calculated quantum mechanical (near Hartree-Fock) energies and field gradients of ca. 80 ion-water molecule configurations.

In Table I the calculated electric field gradient at the nuclear site of a lithium ion, and its fluctua-

TABLE I.

N	$\langle V_{zz} \rangle_{\text{eq}}$ (a.u.)	$\langle V_{zz}^2 \rangle_{\text{eq}}$ (a.u.)
4	$2.2 \cdot 10^{-4}$	$0.3 \cdot 10^{-4}$
5	$2.9 \cdot 10^{-4}$	$0.5 \cdot 10^{-4}$
10	$-13.0 \cdot 10^{-4}$	$1.1 \cdot 10^{-4}$
50	$23.0 \cdot 10^{-4}$	$1.3 \cdot 10^{-4}$
exp.	—	$0.14 \cdot 10^{-4}$

tion, are shown. The experimental value is calculated with $\tau_c = 10^{-12}$ s. N is the number of water molecules, and the averages are calculated from 200 000 configurations.

The origin of the field gradient at the nuclear site has been discussed by several authors. Hertz [2] means that the dominating contribution to the field gradient comes from the water dipoles in the first hydration shell. Deverell [3], on the other hand, ascribes the distortion of the ionic electron cloud, when colliding with a water molecule, the largest contribution.

By a detailed analysis of the configurations generated in the Monte Carlo procedure, we hope to bring some more light on the problem. So far the results indicate that the water molecules closest to the ion are far from tetrahedrally arranged, thus giving a non-zero contribution to the field gradient at the nuclear site. They also seem to be quite mobile. These findings are in qualitative agreement with suggestions made by Friedman [4].

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A.M.O. Study of Solvent Effects in Substituted Benzene Radical Anions

MAURIZIO GUERRA*

Laboratorio C.N.R. dei Composti del Carbonio, Ozzano Emilia, Italy

FERNANDO BERNARDI

Istituto di Chimica Organica, Viale Risorgimento 4, Bologna, Italy

and GIAN FRANCO PEDULLI

Istituto di Chimica dell'Università, Via Ospedale 72, Cagliari, Italy

In this paper we report the results of a theoretical investigation dealing with the effect of the solvent upon the relative stability of the symmetric (ψ_S) and antisymmetric (ψ_A) electronic configurations of substituted benzene radical anions. The problem has

been investigated using a modified SCF-MO INDO procedure, which includes the solvation effects in the way suggested by Constanciel and Tapia [1].

The computations have been carried out for a series of monosubstituted benzene radical anions (C_6H_5-X)⁻, with $X = OH, CN, CH_3$ and the energy differences $\Delta E = E_S - E_A$ between the energies of the symmetric (E_S) and antisymmetric (E_A) configurations computed for various values of the dielectric constant ϵ are listed in Table I, including also the gas phase situation ($\epsilon = 1$).

The substituents listed above have been chosen because they represent situations where the conjugative interactions are significantly different. We have already shown [2], in fact, that the conjugative effect is the dominant factor that determines the preferential stabilization of one of the two configurations ψ_S and ψ_A , that in the absence of the perturbation due to the substituent are degenerate.

In all cases where the substituent has just the π -type lone pair ($X = OH$) or a filled–unfilled π -system characterized by a high energy HOMO and a low energy LUMO ($X = CN$), there is a largely dominant conjugative interaction that dictates the preferential stabilization. In these cases the solvent plays only a minor role, as shown by the results listed in Table I, since the solvent has not the effect to alter the dominant character of an interaction that is largely dominant in the gas phase.

TABLE I. Energy Differences $\Delta E = E_S - E_A$ (kcal/mole) for Various Monosubstituted Benzene Radical Anions at Various Values of the Dielectric Constant ϵ .

Substituent	$\epsilon = 1.0$	$\epsilon = 5.0$	$\epsilon = 20$	$\epsilon = 80$
OH	7.99	12.27	14.12	14.43
CN	-13.86	-13.99	-14.54	-14.97
CH ₃	-4.75	1.47	2.94	3.81

However, when there is not a largely dominant interaction as in the case of $X = CH_3$, where the HOMO is at low energy and the LUMO at high energy, the effect of the solvent can become critical. In this case, our computations show that ψ_A , that is less stable than ψ_S in gas phase, becomes more stable when the medium has a dielectric constant greater than ~ 3.5 and the trend becomes more pronounced with the increase of the dielectric constant.

Radical anions are known for all the compounds we have examined, except phenol which may be compared with anisole [3]. The experimental results agree well with our computational results, not only for the radical anions of phenol and benzonitrile [4],