Ab initio Molecular Orbital Calculations on the Pyrazine-Lithium Ion Pair

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The results of *ab initio* molecular orbital calculations are presented for the pyrazine$^-$/Li$^+$ ion pair. It is shown that the lowest energy conformation is where the lithium occupies a position in the plane of the pyrazine ring, along the C_2 axis passing through the nitrogen atoms.

Introduction

The association of hydrocarbon anions with alkali metal cations in solvents of low dielectric constant such as tetrahydrofuran have been known for some time, and studied experimentally by Electron Spin Resonance (ESR) [1, 2]. It is convenient to divide these complexes into three classes: the weakly associated "ion pair" type such as naphthalene$^-$/Na$^+$ whose ESR spectrum is markedly temperature and solvent dependent, the strongly associated complexes like *m*-dinitrobenzene$^-$/Na$^+$ whose ESR spectrum is little affected by temperature or solvent changes, and finally the type intermediate between these two extremes, typified by the pyrazine$^-$/alkali metal cation systems. It is with the latter that the present publication is concerned.

Pyrazine$^-$/alkali metal cation system have been extensively studied experimentally: thus, Atherton [3] has studied the association of pyrazine$^-$/Li$^+$, McDowell and Paulus [4] have studied pyrazine$^-$/Na$^+$, whilst Santos-Veiga and Neiva-Correia [5] have studied the association of pyrazine$^-$ with K$^+$.

A number of observations can be made from the ESR spectra, in particular the hyperfine coupling constant due to the cation. This has been interpreted as arising from "contact" ion pairs not separated by solvent molecules [6].

There has been a certain amount of speculation as to the electronic structure of these complexes, but little theoretical work has been reported. Claxton [7] has performed extended Hückel calculations on the monoprotonated pyrazine radical, and found that the proton should be located in the plane of the pyrazine ring on the C_2 axis passing through the nitrogen atoms. However, pyrazine$^-$/H$^+$ has not been observed experimentally, and a more interesting system is pyrazine$^-$/Li$^+$. Atherton and Goggins [3] calculated the electrostatic potential by evaluating the nuclear attraction integrals of the charge distribution of pyrazine anion for a point positive charge. On the basis of their calculation they suggested that the

Li^+ was located around the nitrogen atoms. In a later publication, Atherton [8] used perturbation theory to try to assess the relative importance of charge transfer states arising from π and from n pyrazine orbitals to the $2s$ orbital of lithium. He suggested that the Li^+ was probably located above the ring, but could draw no definite conclusion, whilst Claxton [9] found that, using both extended Hückel and CNDO/2 treatments, the Li^+ should be located above the *centre* of the pyrazine ring. His calculations failed to explain the observed ESR spectrum, and he concluded that if the Li^+ were situated in the region of the lone pair nitrogen electrons, all the results would be satisfactory.

In this publication we present the results of a series of *ab initio* molecular orbital (MO) calculations on the electronic structure of the pyrazine$^-$/Li^+ ion pair, and show that the Li^+ is indeed predicted to lie in the plane of the ring along the C_2 axis passing through the nitrogen atoms.

Calculations

The MO calculations were performed using a basis of Gaussian type orbitals (GTO's) contracted to approximate to a minimal Slater type orbital (STO) basis. Each STO was approximated as a contraction of 4 GTO, and GTO exponents and expansion coefficients being taken from the literature [10]. The STO exponent of hydrogen was taken as 1.2 and an STO basis of $1s$, $2s$, $2p_x$, $2p_y$, $2p_z$ orbitals was used for carbon nitrogen and lithium. Thus 156 GTO were contracted to 39 STO.

The calculations were performed in part using a version of IBMOL 4 which had been partially rewritten in the ICL assembler language PLAN for the University of Manchester ICL 1906A computer. The "symmetry list" facility of POLYATOM was also added to this program, which has been described elsewhere [11]. The remaining calculations were performed on the University's CDL 7600 computer using a version of POLYATOM 2 [12]. It should be mentioned that both suites of programs were compared against each other, and gave identical answers.

The coordinates of the atomic nuclei are given in Table 1; the lithium atom was assumed throughout to be in the plane containing the nitrogen atom and perpendicular to the ring. Three sets of calculations were performed with the

Table 1. Geometry of complex ($a_0 = 0.52916$ Å). α, β, γ were varied to find the lowest energy

Atom	X/a_0	Y/a_0	Z/a_0
H_1	0	-3.995	-2.344
H_2	0	-3.995	2.344
H_3	0	3.995	2.344
H_4	0	3.995	-2.344
N_1	0	0	-2.589
N_2	0	0	2.589
C_1	0	-2.210	-1.314
C_2	0	-2.210	1.314
C_3	0	2.210	1.314
C_4	0	2.210	-1.314
Li (a)	0	0	α
Li (b)	β	0	-2.589
Li (c)	γ	0	0

Table 2. Hyperfine coupling constants/gauss. The experimental signs are inferred for the anion, where the experimental results are given in parentheses [14]

	Anion	(a)	(b)	(c)
C_1	−2.02 (−2.88)	+4.71	+2.94	−1.07
C_2		−6.22	−5.17	−1.07
N_1	−6.84 (−7.21)	−2.86	−3.64	−4.72
N_2		−5.58	−5.23	−4.72
H_1	−0.37 (−2.64)	−7.56	−5.04	−0.81
H_2		+5.75	+4.64	−0.81
Li		−0.61	−0.69	−0.36

lithium (a) in the plane of the ring, (b) vertically above one of the nitrogen atoms, and (c) vertically above the centre of the ring. For each set, a series of calculations was performed with the lithium atom at different positions along the relevant axis, as can be seen from Table 1.

To speed up the computation of the many two electron integrals, many of which are common for each of the different calculations, the following procedure was adopted (a) all two electron integrals involving orbitals centered on pyrazine were calculated, (b) for each different lithium position, the integrals involving at least one orbital centred on lithium were calculated and the two lists of integrals merged together. The one electron integrals, which are relatively trivial, were recalculated each time.

Self consistent field wavefunctions were obtained using the Unrestricted Hartree Fock (UHF) method [13]. Some initial difficulties were encountered in obtaining convergence, but saving the density matrices $R^{(p)}$, $R^{(p+1)}$ from two successive cycles $p, p + 1$ of the iterative procedure and using the simple extrapolation procedure

$$R^{(p+2)} = \lambda R^{(p+1)} + (1 - \lambda) R^{(p)}$$

with $\lambda = 0.5$ usually guaranteed fairly rapid convergence. In addition, for each set of Li positions the UHF density matrices from one run were used as input data for the remainder in the series.

Results and Conclusions

The variation of total energy (electronic + nuclear) with α, β, γ is shown graphically in Fig. 1. Here, α/a_0 is the Z coordinate of the Li atom for configuration (a), β/a_0 and γ/a_0 the x coordinates of the Li atom for configurations (b) and (c) respectively (see Table 1). The graph for configuration (a) shows a reasonably well defined minimum, whilst the graphs for (b) and (c) have very shallow energy minima, particularly (c). The optimum values of α, β, γ are

$$\alpha = 5.8 \, a_0 \quad E = -268.61770 \, e^2/a_0,$$
$$\beta = 3.5 \, a_0 \quad E = -268.59480 \, e^2/a_0,$$
$$\gamma = 3.2 \, a_0 \quad E = -268.58148 \, e^2/a_0,$$
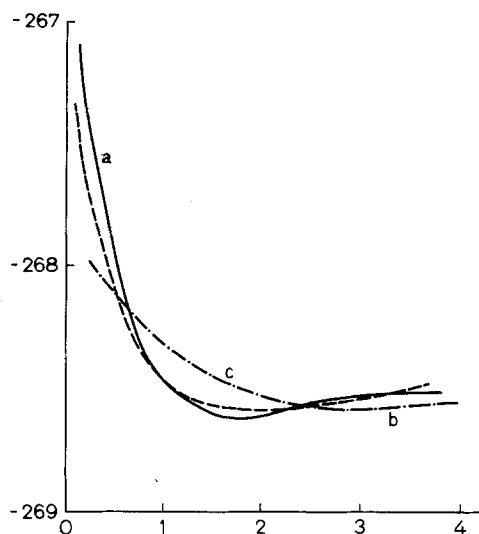
where e is the charge on the electron.

Fig. 1. Variation of electronic energy in atomic units with position of Li for the three configuration a, b and c. The x axis represents, in atomic units, a $Z_{Li} - 4.0$, b $X_{Li} - 1.5$, c $X_{Li} - 0.5$
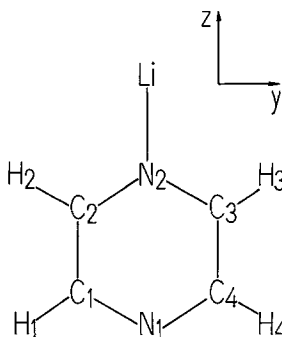

Fig. 2. The lowest energy configuration of the pyrazine$^-$/Li$^+$ ion pair. The Li$^+$ atom lies 3.211 atomic units from the nearest N atom, along the C_2 axis passing through the nitrogen atoms

The energies are very similar, but nevertheless the Li$^+$ is predicted to lie in the plane of the ring along the C_2 axis passing through the nitrogen atoms, as shown in Fig. 2.

The fact that such small energy differences are involved presumably explains the erratic results reported previously [8, 9].

We have also attempted to calculate the ESR spin coupling constants for the complex, and for pyrazine$^-$. In the case of pyrazine$^-$, the ^{13}C and ^{14}N coupling constants agree extremely well with the experimental values, whilst the proton coupling constant agrees badly with the experimental result. This is not entirely unexpected, due to the poor representation of a hydrogen $1s$ orbital by GTO. For the complex, Atherton and Goggins [3] reported that the Li gives a coupling constant of 0.70 gauss, 1.98 and 3.33 gauss for the protons, and 5.36 and 8.68 gauss for the nitrogens. They did not report ^{13}C splittings. It is difficult to draw any

concrete conclusions from our coupling constant calculation: the ^{14}N coupling constants agree badly with experiment, and the proton ones are equally unreliable. The interpretation is also made difficult by the fact that the UHF wavefunction for (a) and (b) contains a large amount of spin contamination even after spin annihilation; $\langle S^2 \rangle_{aa} = 0.90$ [13] for (a) and (b) whereas $\langle S^2 \rangle_{aa} \approx 0.75$ for case (c).

Nevertheless, on the basis of the energy calculation we feel confident that the Li^+ does lie in the position predicted by our calculation. A preliminary series of calculations using a different contraction (2 GTO/STO) gave a similar result, so we are reasonably confident that the result is not "basis set dependent".

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