The zwitterionic and diradical character of sulphobetaines

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We have carried out MNDO type theoretical calculations on two forms of sulphobetaine molecules. The zwitterionic form is described for both cases and a discussion of a possible open shell state is presented. The discussion shows that a diradical state is a possible option in polymerization.

(Keywords: sulphobetaines; zwitterions; diradicals; vinyl pyridine derivatives; synthesis; polymerization)

INTRODUCTION

A theoretical analysis of zwitterionic derivatives of vinyl pyridines, i.e. carboxylic betaines, has recently been reported[1]. In that study, calculations of the closed shell molecules and the corresponding free radicals allowed us to suggest possible free-radical pathways for polymerization. It was also mentioned that this reaction process takes place too fast to be experimentally analysed and thus compared with the theoretical predictions. In this work we have chosen a similar system involving sulphobetaine compounds but with which experimental analysis can be carried out. These species can be synthesized by a reaction between the vinyl pyridine and propane or butane sultone. The reaction provides several stable structures amenable to experimental studies.

The zwitterionic character of this kind of molecule has been demonstrated previously[2] and their behaviour arises from the saturation of nitrogen's Lewis octet. As a consequence of the charge distribution, interesting properties are observed with respect to the dilute solution behaviour and solid state characteristics of the polymeric derivatives. Aqueous solutions including this type of compound[3] show an increase in the ionic strength which had led to applications in tertiary oil recovery[4].

As in the case of the carboxylic betaines, the analysis of the zwitterionic character of sulphobetaine compounds is used to elucidate possible reaction pathways. A knowledge of the orientation of the charges within the molecule is an important aspect of this study. An interesting result shows that in addition to the zwitterionic character a diradical form is also possible. The theoretical analysis provides evidence of this state, and this suggests interesting possibilities for additional pathways.

METHOD

All calculations were performed using the MNDO method[5] from the MOPAC software[6] using different keywords depending on the desired description. Optimization of the geometry was carried out in all cases. The program was compiled in an IBM 4381 computer with standard parameters[7]. The initial geometry for the closed shell molecules was obtained using the molecular mechanics MMX method[8].

RESULTS AND DISCUSSION

Description of ground state molecules

The molecules were two analogues corresponding to the structure shown in *Figure 1*. The difference between these molecules lies in the number of carbon atoms in the chain. Compound I contains two carbon atoms between the nitrogen and sulphur atoms and compound II contains four carbon atoms. One of the purposes of this study was to investigate the influence of the carbon chain length on the chemical behaviour.

Figure 2 shows the magnitude of the net charges and σ–π electronic populations obtained from the Mulliken analysis. As observed, the chain length drastically affects the magnitude of the dipole moment, with values of 7.9×10^{-29} C m for compound I and 11.7×10^{-29} C m for compound II. Consequently, a larger ionic strength is produced in aqueous solutions of the derivatives of compound II than for the corresponding solutions of the derivatives of compound I. Moreover the difference in the dipole moment between both structures affects the chain expansion in aqueous solutions, and this has been observed in the corresponding intrinsic viscosity measurements[9] of the saline solutions of these materials. On the other hand, experimental data of conductivity of

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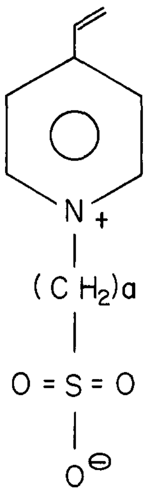

Figure 1 Molecular structure of the two analogues

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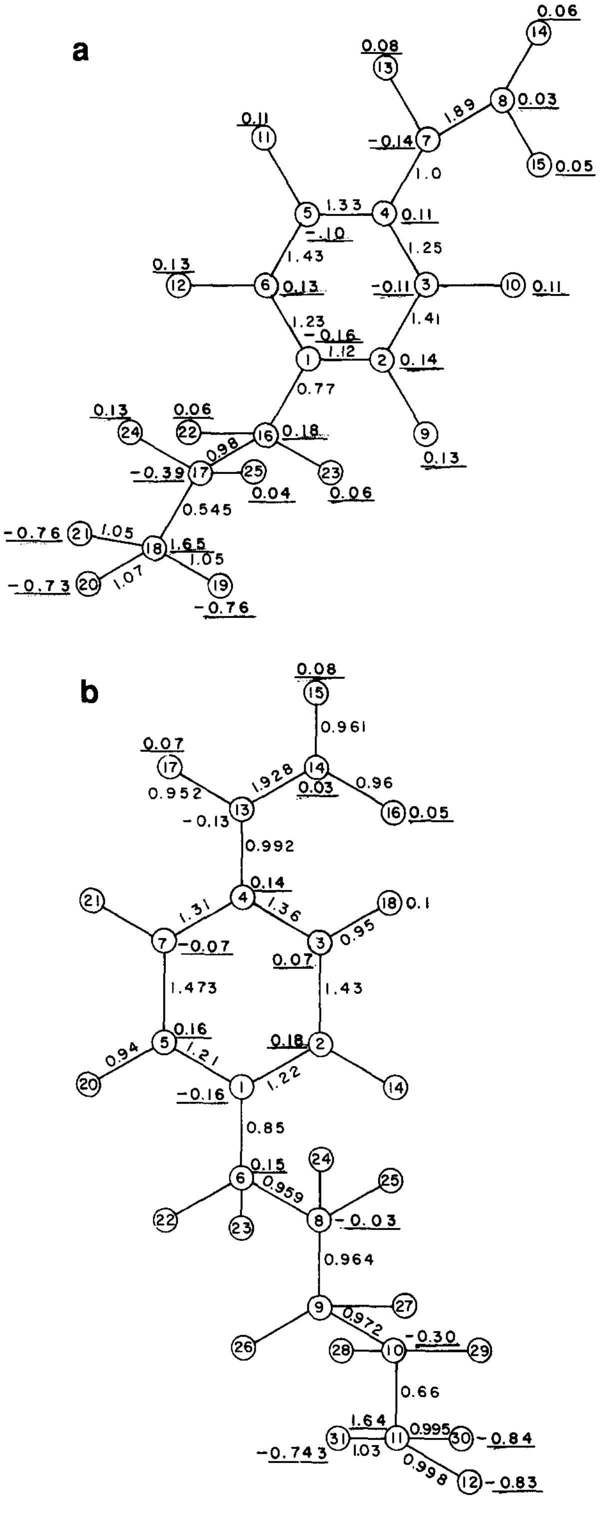

Figure 2 Magnitude of net charges and σ–π electronic populations. (a) Compound I: heat of formation, $\Delta H_f = 164.129$ kcal mol^{-1}; total energy, $U = 2698.93$ eV; ionization potential, IP = 9.2 eV; dipole moment, $\mu = 7.9 \times 10^{-29}$ C m. (b) Compound II: $\Delta H_f = 139.731$ kcal mol^{-1}; $U = 3011.172$ eV; IP = 8.143 eV; $\mu = 11.7 \times 10^{-29}$ C m

solid solutions of sulphobetaine polymers with mineral salts, have shown that the increase in chain length alters the value of ionic conductivity from 6.7×10^{-6} to 4×10^{-4} S cm^{-1} (ref. 10). This is a large change directly related to the difference in values of the dipole moments. There is additional evidence, provided by TEM studies on these polymers[11], which suggests the formation of clusters due to the strong interactions of dipoles.

Koopman's theorem ionization potentials were obtained. The difference in charge distribution between both molecules produces important differences in these ionization potentials; the values are 9.2 eV and 8.1 eV for structures I and II respectively. Apparently the first ionizable electron is located in an electron-rich zone, such as the aromatic ring or the region around the sulphonate group where the charge is delocalized. However, the bond order analysis shows that the electron is located on the carbon atom close to the sulphur atom, which has a large negative charge. The size of this charge is larger for compound I than for compound II, and this explains the difference in the ionization potentials.

The HOMO and LUMO regions are similar for both species, and are represented in *Figure 3*. The HOMO level is comprised of a combination of the atomic orbitals from the sulphur atom, the carbon atom attached to it and the delocalized negative charge of associated oxygen atoms.

The LUMO level is a classical combination of the π orbitals of the aromatic ring, but gives the unexpected result that the electron-rich zone is at the same time a region of charge withdrawal. This is due to the presence of the delocalized positive charge of the quaternized nitrogen.

The charge and σ–π populations in *Figure 2* provide evidence of possible chemical attack sites. A nucleophilic attack might take place on the chain carbon atom close to the ring and such a reaction has a strong possibility of leading to chain scission. An electrophilic attack is expected in the position of the negatively charged oxygen atoms or on the chain carbon connected to the sulphur atom. The vinyl group appears to be inert in these reactions.

Diradicals

An assessment of the reactivity of the sulphobetaine monomers and possible reaction pathways for polymerization is an important aspect of this work. Initially a study of possible reaction paths including free radicals was considered. Indeed numerous attempts failed to reach a stable configuration using an open shell and a

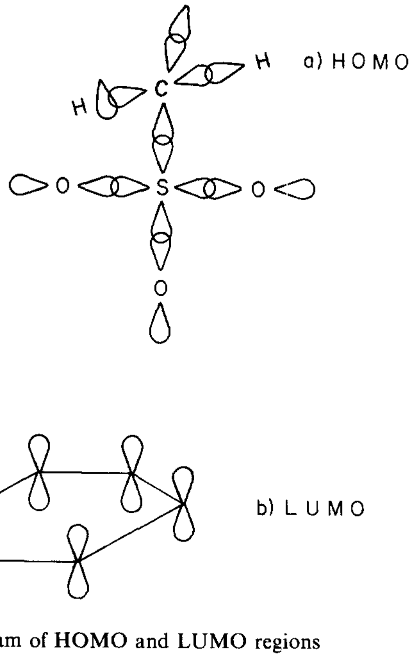

Figure 3 Diagram of HOMO and LUMO regions

self-consistent field sytem with an odd electron could not be obtained. Attempts to find a possible cause for this unexpected instability led us to undertake an independent calculation with the same software to verify the electron distribution within the valence shell of compound II, varying the multiplicity of the system. We found a stable structure with a multiplicity of three, implying a diradical structure. Using this particular structure it was possible to achieve a stable open shell model and this gave the possibility of a new reaction pathway.

Salem and Rouland[12] have shown that the term diradical is used loosely to describe systems which can be formally expressed with two unpaired electrons. These electrons can have parallel spins and in this case form the so-called triplet state. It has also been suggested that it is responsible for phosphorescence and has been invoked in photochemical reactions of polymerization[13]. Furthermore it has been proposed that this is an alternative structure for a zwitterion[12]. Basically the terms diradical and zwitterion are generalizations of a true situation, since the zwitterionic state involves some ionic character and the diradical state involves some covalent character.

It has been proposed that the precursors for polymerization are sometimes diradicals rather than zwitterions[14], since these species are much less stable and more short-lived than the zwitterions, and polymerization is the preferred trapping method for such radicals. As Hall and Padias[15] have pointed out in their study of tetramethylenes, the nature of these compounds can vary from a non-polar diradical to a polar diradical and finally to a zwitterion.

It is common to find an association between the zwitterionic and the diradical state[12], and since in our case this association exists, we carried out a new set of calculations on the diradical species, taking into account the triplet state. The results yield a large energy difference (3.361 eV) between the diradical and zwitterionic structure, where the latter is thermodynamically favoured. This shows that it is necessary to provide energy to reach the radical state, and only when this state is attained can the polymerization reaction take place.

A schematic representation of the diradical with a triplet state is shown in *Figure 4*. This configuration includes two electrons in distinct molecular orbitals with an energy difference of 0.612 eV between the HOMO and the preceding molecular orbital, obviously with no degeneracy. The difference between the HOMO and the LUMO is 2.17 eV.

There are other differences between the zwitterionic and the diradical molecules. In the latter the HOMO and the preceding orbital are formed by the delocalized charge of the oxygen atoms and the charge on the carbon atom attached to the sulphur atom. The LUMO is comprised of the combination of atomic orbitals of carbon atoms of the vinyl group and those of the ring. The energy difference between the HOMO and the LUMO is relatively small (2.17 eV) and consequently an electrophilic attack on the empty LUMO is possible.

This low energy barrier suggests a free-radical pathway for a polymerization reaction, since it is equivalent to the energy of yellow light, i.e. it is possible to induce the reaction with heat or visible light. Additionally an anionic mechanism, as shown in *Figure 5*, is an interesting alternative which will be discussed in a future paper.

Strictly speaking, the diradical species are not energetically favourable. Indeed, the heat of formation of the calculated structure (910.24 kJ mol^{-1}) is high but it is possible to reach this value under laboratory conditions.

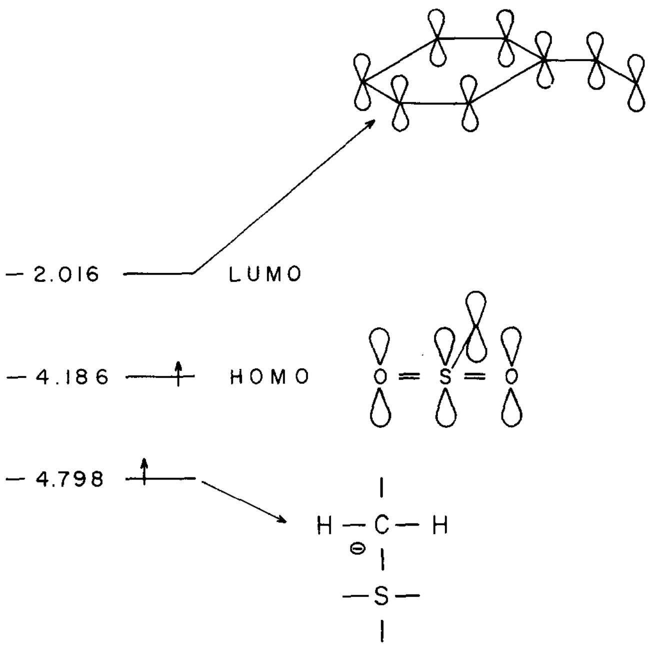

Figure 4 Diagram of diradical with a triplet state

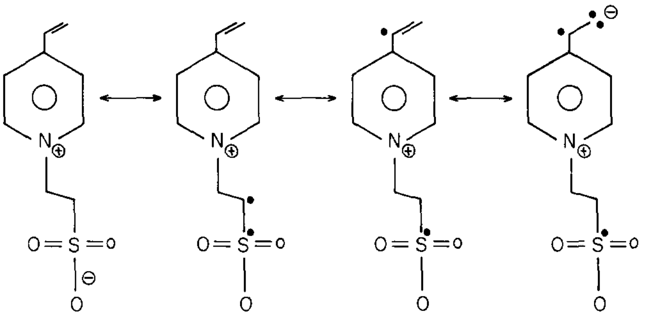

Figure 5 Proposed mechanism for the formation of a reactive anionic structure

CONCLUSIONS

This result is useful in explaining some experimental features of polymerization. The usual synthesis procedures for these compounds is carried out in two ways. The first method is polymerization of 4-vinylpyridine, followed by the quaternization reaction[16–18]. The second method consists of a free-radical pathway; our results offer alternative explanations for the mechanism of this type of reaction.

Free-radical polymerization is a common reaction pathway to synthesize sulphobetaine derivatives. In our analysis, we have shown that the precursor monomer is not a classical odd-electron species, but a diradical one.

This analysis has provided evidence of this state through theoretical calculations using the MNDO method.

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