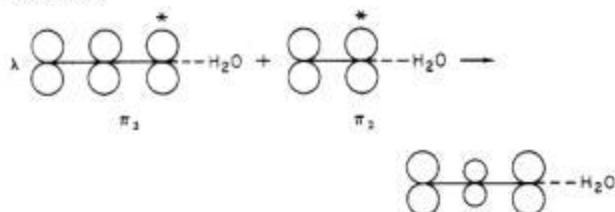


Scheme I



constraint was removed and the optimization of the angle formed by the plane of the water molecule and the plane of the ion was performed starting with a 90° angle, a minimum in energy was obtained for an angle of 70° . The energy corresponding to this angle however proved to be higher in value than the energy of the structure having the ion and the water molecule(s) coplanar. In all cases at least one hydrogen was constrained to be in the plane of the molecule.

When the optimization is performed on the bond lengths and angles of hydrates, the results indicate no change for the N-O angle, in accordance with the results of Banerjee et al.¹⁴ The water molecule's geometry is kept frozen at the experimental values because of the reasons given previously. The N-O bond length's changes fall into the following pattern: when a water molecule is attached to one of the oxygen atoms of the ion, it has the effect of leaving unchanged or slightly lengthening the N-O bond length involved. The remaining N-O bonds are shortened in some cases (to 1.24 Å). The explanation for this could be found by looking at the electrostatic effects. When the positively charged H atom of the water molecule forms a hydrogen bond with the oxygen, it draws the electronic density forward, increasing its net negative charge. This electron cloud shift weakens and lengthens the N-O bond, while the remaining bonds are strengthened and shortened. To test the electrostatic charge influence on the bond lengths of the NO_2^- ion, we investigated the change produced by a negative charge represented by F^- at a distance of 2 Å from the oxygen. Indeed, the N-O bond decreased this time while the other N-O bond increased (1.22 vs. 1.33 Å). When the reverse was tried, by setting the Li^+ ion at a distance 2 Å from the oxygen, the reversed trend was observed (1.31 vs. 1.20 Å). An alternative explanation for these changes could be found via perturbation theory.

Bringing a positively charged atom (H of H_2O) into the vicinity of one of the oxygens will increase the "electronegativity" of that atom, resulting in an increase in its negative charge.

Using the π orbitals of NO_2^- as an example, we see that the virtual antibonding orbital, π_3^* , will mix into the non-bonding π_2 so as to increase electron density on the starred oxygen (see Scheme I).

The resultant orbital shows decreased N-O* bonding and increased N-O bonding, along with a buildup of negative charge on the starred oxygen and a decrease on the unstarred. The reverse holds true if a negative charge is brought into the vicinity of the starred oxygen and the mixing coefficient, λ in Scheme I, will change sign.

The changes in energy due to the optimization of the N-O bond lengths in the hydrates are less than 0.5 kcal/mol. The energies displayed in Table II and Figures 1-8 correspond to the systems with the N-O bond lengths kept at 1.26 Å.

The structures of type i proved to be nonbinding, precluding formation of a purely electrostatic bond. For the other structures, the binding energies displayed in Table II show a decrease with the addition of each water molecule. The experimental numbers obtained for the binding free energy by Fehsenfeld and Ferguson² are 6.8 kcal/mol for $\Delta G_{0,1}$, 5 kcal/mol for $\Delta G_{1,2}$, and 3.4 kcal/mol for $\Delta G_{2,3}$ for the $\text{NO}_3^-(\text{H}_2\text{O})_n$ clusters, while for the $\text{NO}_2^-(\text{H}_2\text{O})_n$ clusters they report $\Delta G_{0,1}$ as 8 kcal/mol, $\Delta G_{1,2}$ as 5.9 kcal/mol, and $\Delta G_{2,3}$ and 4.0 kcal/mol. Other theoretical calculations follow the same trend as experimental ones. Since we estimate the ΔE of binding, a meaningful comparison with the experimental ΔG can be made only in a very qualitative way. On the other hand, the experimental values of Payzant et al.¹⁰ for $\Delta H_{n-1,n}$ where $1 \leq n \leq 3$ for the $\text{NO}_2^-(\text{H}_2\text{O})_n$ clusters and $n = 1$ for the $\text{NO}_3^-(\text{H}_2\text{O})_n$ clusters compare fairly well with our values for the E of binding as seen in Table II.

In conclusion, the hydrates examined feature binding energies which decrease with the addition of each water molecule. The NO bonds which are involved in hydrogen bonding with a water molecule are lengthened while the others are shortened. The structures which exhibit double hydrogen bonding between the water molecule and the ion prove to be more stable than the ones on which the linearity of the hydrogen bonds is imposed as a constraint.

Nuclear Magnetic Resonance Spectroscopy Studies of Nematic Liquid Crystals. 2. *trans*-4-Alkyl(4-cyanophenyl)cyclohexanes

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NMR has been employed to measure the orientational order parameters for the nematogenic homologous series *trans*-4-alkyl(4-cyanophenyl)cyclohexanes by studying the dipole-dipole splittings. The values of the order parameters are compared with those obtained by optical studies.

Introduction

It is very well established that the order parameters of liquid crystals govern most of their physical properties.^{1,2}

Many investigations employing various techniques of the order of arrangement in nematic liquid crystals are reported in the literature.³⁻⁷ The nematogenic compounds

(1) de Gennes, P. G. "Physics of Liquid Crystals"; Clarendon Press: Oxford, 1974.

(2) Chandrasekhar, S. "Liquid Crystals"; Cambridge University Press: Cambridge, 1977.