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Anion–molecular interaction through CH_3 groups: Model *ab initio* studies

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Abstract. 3–21*G*, 6–31*G* and 6–31 + *G* calculations have been performed on $Cl^-...H_3CCl$ and $LiCl...H_3CCl$ complexes with two different configurations each. Optimized geometries, stabilization energies, CH force constants and harmonic vibrational frequencies for CH_3Cl and its complexes are reported. Comparison of the calculated frequency shifts of CH-stretching bands of CH_3Cl, on complexation, with experimental results of related systems indicate that the interaction of Cl^- with CH_3 group takes place in a linear manner with the CH bond. A lower frequency shift for $LiCl...H_3CX$ with reference to the $Cl^-...H_3CX$ complexes is explained on the basis of the reduction of the basicity of Cl^- ion in the presence of counter ion in the former complex considered.

Keywords. Anion–molecular interaction; model *ab initio* studies; methylchloride complexes.

1. Introduction

Anion–molecular interactions have been studied by various methods (e.g. Parker 1962; Marcus 1985) in protic and aprotic solvents. It is, in general, found that anions are more solvated by protic solvents while cations show significant solvation by strong electron donors. Anion solvation in protic solvents is dominated by ion–dipole interactions and hydrogen-bond interactions, whereas in dipolar aprotic solvents, in addition to the ion–dipolar interactions, those due to the natural polarizability of anions and dipolar solvents also make significant contribution. Since smaller anions show stronger hydrogen bonding and larger anions show higher natural polarizability, the order of the strength of anion–molecular interactions, as a function of the size of the anion, is found to be reverse in nature for protic and aprotic solvents. Because of the lesser extent of solvation of anions by dipolar aprotic solvents the nuclear substitution reactions by halide ions are found to be faster in these solvents where the anions are fairly 'naked'. The extent of solvation of anions by protic and aprotic solvents is also reflected in the values of limiting anionic conductances in different media.

Vibrational spectroscopic investigations on solutions of alkali metal halides and tetraalkyl ammonium halides in dipolar aprotic solvents (Perelygin 1962; Pominow and Gadzhiev 1965; Janz *et al* 1967; Roche and Huong 1970; Oliver and Janz 1970; Coetzee and Sharpe 1972; Sadlej 1979; Marcus 1985; Miyaji and Morinaga 1986; Ramana and Singh 1988, 1989; Jayaraj and Singh 1993) indicate the importance of the involvement of the CH_3 group of aprotic solvents in such interactions. It is found

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(Roche and Huong 1970; Coetzee and Sharpe 1972; Ramana and Singh 1988, 1989) that interaction of halide ions with acetonitrile (AN) and dimethyl sulphoxide (DMSO) leads to the development of a low frequency component in the CH stretching band. We thought it of interest to carry out *ab initio* MO calculations on model systems for anion–molecular complexes to get an idea about the mode of such interactions. Calculations on 3–21*G*, 6–31*G* and 6 – 31 + *G* levels have been carried out on CH_3Cl, $Cl^-...H_3CCl$ and $LiCl...H_3CCl$ species and the optimized geometries, stabilization energies and vibrational frequency parameters for the CH stretching mode of CH_3Cl are reported.

2. Computational details

Ab initio MO calculations were carried out using the Gaussian 88/90 package (Frisech *et al* 1984) for both geometry optimization and vibrational analysis. Calculations were carried out using a gradient algorithm contained within the program. Optimization in each case is carried out using supermolecular approach where all the geometrical parameters of complexes were allowed to relax. The calculations were performed on VAX/MS version V5·3-1 computer.

3. Results and discussion

In figure 1 are shown the structural parameters for the five species considered for calculations. Geometrical parameters and stabilization energies are given in table 1.

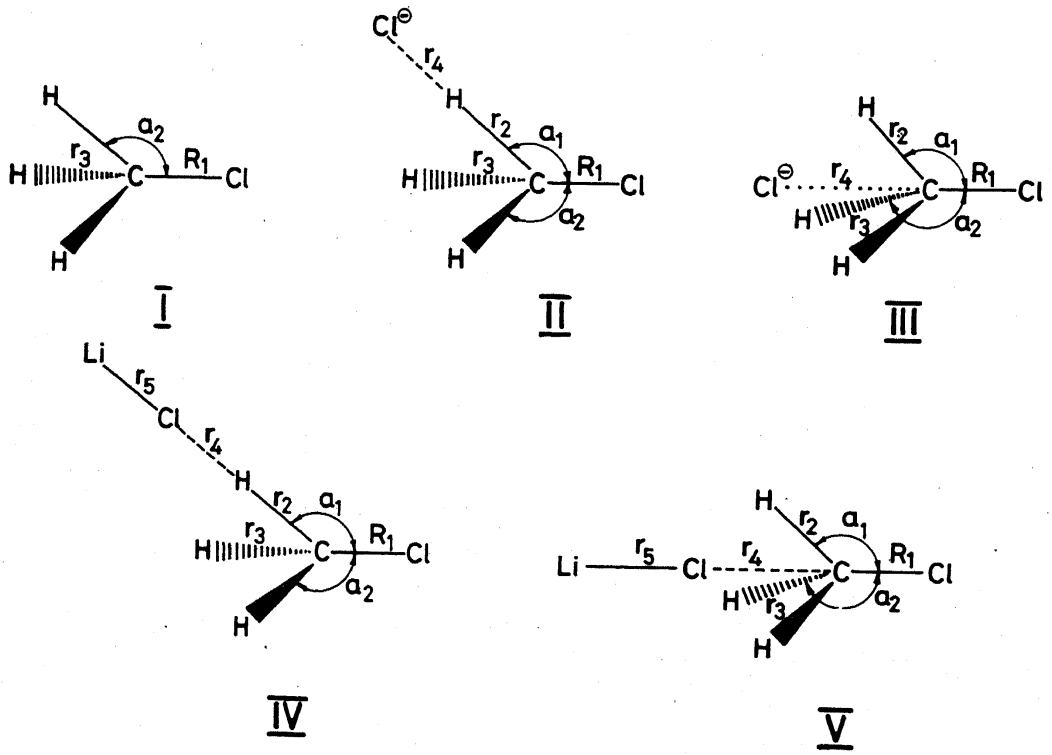

Figure 1. Geometrical parameters for complexes of methyl chloride with Cl^- and LiCl.

Table 1. Geometrical parameters and stabilization energies for CH_3Cl, $Cl^-...H_3CCl$ and $LiCl...H_3CCl$ as obtained by 3–21*G*, 6–31*G* and 6–31 + *G ab initio* calculations; bond distances in Å, bond angles in degrees and ΔE in kcal/mol.

Structure		R_1	r_2	r_3	r_4	r_5	a_1	a_2	d_1	$-\Delta E$
I	3–21*G*	1·8919		1·0737				106·23	120·00	
	6–31*G*	1·8634		1·0735				107·01	120·00	
	6–31 + *G*	1·8643		1·0735				106·96	120·00	
II	3–21*G*	1·9182	1·0822	1·0744	2·4167		108·38	104·50	120·88	11·2701
	6–31*G*	1·8871	1·0802	1·0744	2·5002		108·91	105·40	120·77	31·8289
	6–31 + *G*	1·8852	1·0779	1·0741	2·5818		108·95	105·50	120·67	7·6867
III	3–21*G*	1·9744	1·0673	1·0690	3·0643		106·80	104·38	120·06	14·1416
	6–31*G*	1·9286	1·0679	1·0695	3·1982		107·37	105·62	119·99	34·9469
	6–31 + *G*	1·9226	1·0686	1·0698	3·2987		107·12	105·74	119·96	10·8655
IV	6–31*G*	1·8716	1·0732	1·0738	2·8046	2·1217*	107·44	106·43	120·29	2·7153
	6–31 + *G*	1·8728	1·0731	1·0736	2·8012	2·1092*	107·45	106·40	120·30	3·3068
V	6–31*G*	1·8787	1·0712	1·0721	3·5533	2·1232	107·23	106·80	119·98	3·4121
	6–31 + *G*	1·8806	1·0709	1·0720	3·5442	2·1103	107·23	106·72	119·98	4·2087

*The corresponding values for LiCl are 2·1167 and 2·1103 respectively

It is found that the stabilization energies for $Cl^-...H_3CCl$ calculated by 6–31*G* basis set are higher than those calculated by 3–21*G* and 6–31 + *G* basis sets. This is in line with our previous observations (Singh and Knoezinger 1992; Mohandas *et al* 1993) where it is found that for anion–molecular interactions using higher basis sets, diffused functions must be used for better results. It is found that the interactions do not affect the bond distances and bond angles significantly, however, the changes are higher for interactions with Cl^- than with LiCl. The stabilization energies are found to be higher for configurations where CH_3Cl interaction takes place along the Cl–C bond.

As mentioned above, Coetzee and Sharpe (1972), Roche and Huong (1970) and Ramana and Singh (1988, 1989) have shown that anion–molecular interactions result in a shift in the CH-stretching band of the CH_3 group of aprotic solvents to lower frequencies. The perchlorate ion causes no frequency shift although it produces an intensity increase and some broadening of the CH band. Coetzee and Sharpe (1972) observed that CH frequency shifts produced by F^- and Cl^- also depend on the nature of the cation, being significantly smaller for the Li^+ ion than for the tetraalkyl ammonium salts. The dependence of frequency shifts on the nature of the cation is attributed to ion association. It was argued that ion association withdraws electron density from the site of the anion at which the solvent interacts, with the result that the extent of solvation decreases. Thus alkali metal halides dissolved in aprotic solvents result in solvated contact ion pairs whereas tetraalkyl ammonium halides result in pure anion solvation. The effect of the nature of the cation on the frequency shift of the CH band was explained on the basis of the strength of the ion pair; thus the tighter the ion pair, the smaller the anion-induced frequency shifts. Tetraalkyl ammonium perchlorate was found to have no effect on the CH stretching frequency whereas tetraalkyl ammonium halides caused higher frequency shifts than alkali metal halides. Ramana and Singh (1988, 1989) reported the low frequency component in the CD stretching region in the Raman spectra of solutions of tetraalkyl ammonium halides and alkali metal halides in AN(d_3) and DMSO(d_6). Since solutions of these salts in nitromethane (NM) did not show low frequency CH-stretching bands it was concluded that interaction of halide ions with NM is weak. Solutions of AN and tetraalkyl ammonium bromide in NM with varying concentrations of AN were employed for calculation of equilibrium constant of the anion molecular complex. An equilibrium constant of $0{\cdot}4\,l\,mol^{-1}$ was evaluated for $Br^- + CH_3CN \rightleftharpoons Br^-...H_3CCN$. Addition of small amounts of water to the two- and three-component systems of solutions of tetraalkyl ammonium bromide in AN and AN + NM mixtures resulted in the disappearance of the low frequency components of the CD-stretching band indicating that the low frequency CD-stretching component is definitely due to anion–molecular interactions with aprotic solvents which disappears on addition of water because of stronger interactions of Br^- with water.

In table 2 are summarised results on the calculated harmonic stretching frequencies and force constants for the CH bond for the model complexes considered. The CH-stretching force constant is found to decrease on interactions with Cl^- along the CH bond and it increases when interactions take place along the Cl–C bond. Similar trends are reflected in the corresponding harmonic frequencies also. The results obtained through the three basis sets show similar trends. These observations rule out the possibility of the existence of the complexes in the form of structure III, where the interaction take place along the Cl–C bond, even though it is found to have

Table 2. Harmonic CH-stretching force constants and frequencies for CH_3Cl, $Cl^-...H_3CCl$ and $LiCl...H_3CCl$ as obtained by 3–21*G*, 6–31*G* and 6–31 + *G* calculations; force constants in mdynes/Å and frequencies in cm^{-1}.

		Force constant		CH stretching frequencies		
					E	
Structure		Free	Bound	*A'*	*A'*	*A''*
I	3–21*G*	6·21		3279·4	3398·0	
	6–31*G*	6·23		3280·1	3407·5	
	6–31 + *G*	6·23		3279·2	3405·1	
II	3–21*G*	6·16	5·86	3192·8	3345·9	3383·5
	6–31*G*	6·18	6·00	3220·4	3364·8	3390·4
	6–31 + *G*	6·20	6·09	3242·1	3379·4	3391·3
III	3–21*G*	6·52	6·43	3331·6	3486·6	3467·3
	6–31*G*	6·54	6·44	3329·5	3493·1	3473·6
	6–31 + *G*	6·50	6·42	3323·9	3466·6	3482·1
IV	6–31*G*	6·22	6·26	3278·1	3402·1	3402·1
	6–31 + *G*	6·21	6·27	3278·4	3419·4	3400·4
V	6–31*G*	6·36	6·30	3299·5	3429·5	3440·3
	6–31 + *G*	6·36	6·30	3300·0	3440·7	3428·8

higher stabilization energy than structure II, where the interaction takes place along the CH bond of the CH_3 group.

Similar calculations were performed on $LiCl...H_3CCl$ (structures IV and V) complex using 6–31*G* and 6–31 + *G* basis sets and the results are given in table 2. Here again, it is found that the CH band shifts to lower frequencies for the structure where the interactions of LiCl contact ion pair take place along the CH bond (structure IV), whereas the band shifts to the higher frequency side when the interaction is along the Cl–C bond (structure V). The frequency shifts are however found to be much smaller when compared to the complexes of Cl^- with CH_3Cl (structure II). The presence of a counter ion in the contact ion pair reduces the basicity of the halide ion, thus decreasing the strength of interaction of the halide ion with solvents which results in a smaller frequency shift of the CH bond for the solvated contact ion pair in comparison to the solvated halide ion. Similar results have also been found in the case of hydrated anions and hydrated contact ion pairs in our studies on $X^-...H_2O$ and $MX...H_2O$ interactions (Mohandas *et al* 1993).

The *ab initio* calculations are known to overestimate the frequency shifts as are also found in the present studies, however, the trends in these values with the varying nature of systems considered can be well utilized for determining the configuration of the solvated species as well as assigning the vibrational bands in the IR and Raman spectra. The trends in the calculated frequencies are in line with the experimental findings on the solvated halide ion and contact ion pairs as mentioned above. In the present studies, for the sake of simplicity of computation, calculations have been made on the $Cl^-...H_3CCl$ interaction and applied to the experimental vibrational spectral results on solvated halide ions in aprotic solvents like AN, DMSO etc. Because of the much weaker interaction of the halide ion with methyl halides the IR and

Raman spectra do not show a significant frequency shift in the CH-stretching band of the methyl group. Experimental work on the NIR spectra of halide ions in CH_3I indicates (Jayaraj and Singh 1993) anion–molecular interactions. Similar to the effect of addition of halide ions on local mode vibrational bands of the CH_3 group in the first overtone spectrum of CH_3CN, the relative intensities of $|200\rangle E/|110\rangle A_1$ bands of CH_3I also vary on addition of halide ions.

4. Conclusions

MO calculations on two configurations considered for $Cl^-...H_3CCl$ complex show that the interactions of Cl^- ion with CH_3Cl take place through the CH_3 group along the CH bond. The CH-stretching frequency for this configuration is found to be lower than for the isolated CH_3Cl molecule whereas it is found to be higher for the configuration where the halide ion interaction takes place along the Cl–C bond. Experimental results on the solutions of halide ions in AN and DMSO are in conformity with the suggested configuration of anion–molecular interactions in aprotic solvents. Lower frequency shifts observed for solutions of alkali metal halides in aprotic solvents in comparison to the frequency shifts observed for halide ions in aprotic solvents are explained on the basis of the calculated values for the $LiCl...H_3CCl$ and $Cl^-...H_3CCl$ complexes.

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