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Conformational Analysis of *N*-Methylpyrrolidine Betaine Hydrochloride by X-Ray Diffraction and *Ab Initio* Calculations

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The structure of the title compound in the solid state and its five most stable conformers in the gas phase have been analysed by X-ray diffraction, and by MP2/6-31G(d,p) and BLYP/6-31G(d,p) calculations, respectively.

We report here the effect of the attractive Coulombic interaction between the two oppositely charged groups in *N*-methylpyrrolidine betaine hydrochloride, MPRBET·HCl, on its conformation in the solid state and the gas phase.

X-Ray Diffraction.—X-Ray data were collected on a KUMA-4 diffractometer. MPRBET·HCl has a monoclinic space group, $P2_1/c$, $Z = 4$, $a = 6.750(1)$, $b = 11.502(2)$, $c = 12.146(2)$ Å, $\beta = 109.36(3)°$, $V = 889.7(3)$ Å^3, $R = 0.036$, CuKα radiation ($\lambda = 1.54178$ Å). The structure was solved by direct methods using SHELXS-86[33] and refined by the SHELXL-93[34] program. Non-hydrogen atoms were located from an E-map and refined anisotropically. The positions of the hydrogen atoms were found from a difference Fourier map, except those of H(31) and H(32), which were located from geometrical considerations. The investigated betaine is protonated and the carbonyl group forms a H-bond with the chloride ion; O···Cl distance is 2.893(3) Å. The nitrogen atom is above the ring carbon atoms and CH_2COOH moiety is in the axial position. The torsion angles of N–CH_2–C–O(H) and the N–CH_2–C=O are 6.5(3) and −174.2(2)°, respectively. Fig. 2 shows a perspective view of MPRBET·HCl and contacts of the chloride ion. The intramolecular N(1)···Cl distance is 5.706(3) Å, while the intermolecular distances are much shorter [4.068(2) Å (symmetry code x; $0.5-y$; $0.5+z$), 4.105(2) (x; $0.5-y$; $0.5+z$), 4.756(2) Å ($1-x$; $-y$; $1-z$) and 4.939(2) Å ($1-x$; $-0.5+y$; $1.5-z$)]. The N^+CH_2COOH moiety is structurally similar to those in other betaine chlorides, with the exception that the oxygen atoms have opposite positions (Table 4).

Ab Initio Calculations.—The *ab initio* calculations were performed with the GAUSSIAN-94 program package.[36] The molecular parameters were optimized at the MP2/6-31G(d,p) and BLYP/6-31G(d,p) levels of theory. Fig. 3 shows the five most stable conformers of MPRBET·HCl. Table 5 gives the dipole moments, total and relative energies. In all conformers (**I**–**V**) the pyrrolidine ring forms an envelope. In conformers **I**, **IV** and **V** the nitrogen atom is above the ring plane while in conformers **II** and **III** the C(3) atom is above the ring plane (Fig. 3).

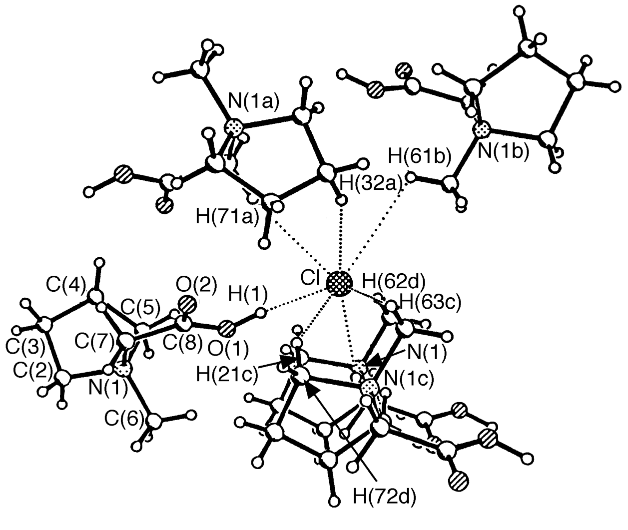

Fig. 2 Perspective view showing contacts of the chloride ion in $C_4H_8N^+(CH_3)CH_2CO_2H{\cdot}Cl^-$

From Table 5, evidently conformer **IV** represents the global minimum in the gas phase. This type of conformer is also the most stable for *N*,*N*-dimethylglycine (DMG).[11] Although, the most stable conformers in MPRBET·HCl and DMG are comparable, they are stabilized by different forces. In DMG the intermolecular N···H–O hydrogen bond is very significant to the stability of the conformers. In MPRBET·HCl the CO_2H group can form a hydrogen bond only with the chloride ion, because the quaternary nitrogen atom has no lone-pair. As Fig. 3 shows, **IV** conformer is stabilized by two interactions, the attractive Coulombic interaction of the chloride ion with the positively charged nitrogen atom and the Cl···H–O hydrogen bond. The electrostatic interactions decrease the proton acceptor properties of chloride ion and as a result a proton transfer takes place in the gas phase. Amines (p$K_a = 10.5$–10.9) with

Table 4 Comparison of X-ray-determined bond lengths (Å), bond angles (°) and torsion angles (°) in some related betaine hydrochlorides

	O(H)···Cl$^-$	C–O(H)	C=O	C–C–O(H)	C–C=O	(H)O–C=O	N–CH_2–C–O(H)	N–CH_2–C=O	Space group
$C_4H_8N^+MeCH_2CO_2H{\cdot}Cl^-$	2.893(3)	1.308(3)	1.204(3)	116.7(2)	118.6(2)	124.7(2)	6.5(3)	−174.2(2)	$P2_1/c$
$Me_3N^+CH_2CO_2H{\cdot}Cl^-$ [a]	2.955(2)	1.316(2)	1.193(2)	109.0(2)	126.0(2)	125.1(2)	173.3(1)	−7.0(3)	$P2_1/c$
$Me_3N^+CH_2CO_2H{\cdot}Cl^-$ [b]	2.946(3)	1.322(4)	1.199(6)	107.9(3)	126.6(3)	125.4(4)	−180.0	0.0	*Cm*
$C_5H_5N^+CH_2CO_2H{\cdot}Cl^-$ [c]	2.928(3)	1.130(3)	1.189(3)	110.4(2)	125.8(2)	123.8(2)	178.6(2)	−1.1(3)	$P2_1/c$
$Et_3N^+CH_2CO_2H{\cdot}Cl{\cdot}2H_2O$ [d]		1.291(6)	1.197(5)	109.6(4)	125.2(5)	125.1(5)	−167.2(4)	13.3(7)	$P2_1/n$

[a] Data from ref. 43; [b] data from ref. 44; [c] data from ref. 45; [d] data from ref. 46.

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Table 5 Total energy (E/hartree[a]), relative energies (E_{rel}/kcal mol^{-1}), dipole moment (μ/debye), selected distances (Å) and dihedral angles (°) for conformers **I**–**V** of the 1-(carboxymethyl)-1-methylpyrrolidinium chloride, MPRBET·HCl

Conformer	E	E_{rel}	μ	O···Cl	N^+···Cl	O···H	H···Cl	O=C–O–H
BLYP								
I	−940.350577	9.42	15.49	2.916	5.735	1.538	1.389	0.0
II	−940.358167	4.46	14.24	2.855	4.569	1.105	1.754	−178.7
III	−940.350442	9.51	16.27	2.922	6.345	1.533	1.393	−41.8
IV	−940.365592	0	10.65	2.977	3.726	1.045	1.946	−169.8
V	−940.350074	9.74	17.03	2.921	6.355	1.532	1.393	0.5
MP2								
I	−938.548967	9.96	15.87	2.947	5.723	1.630	1.326	−1.5
II	−938.555720	5.72	15.13	2.820	4.464	1.065	1.761	−179.9
III	−938.549633	9.54	16.13	2.962	6.259	1.640	1.325	0.02
IV	−938.564831	0	11.43	2.972	3.615	1.014	1.970	−172.9
V	−938.548181	10.45	17.06	2.957	6.277	1.634	1.326	−0.2

[a] 1 hartree = 627.72 kcal mol^{-1}.

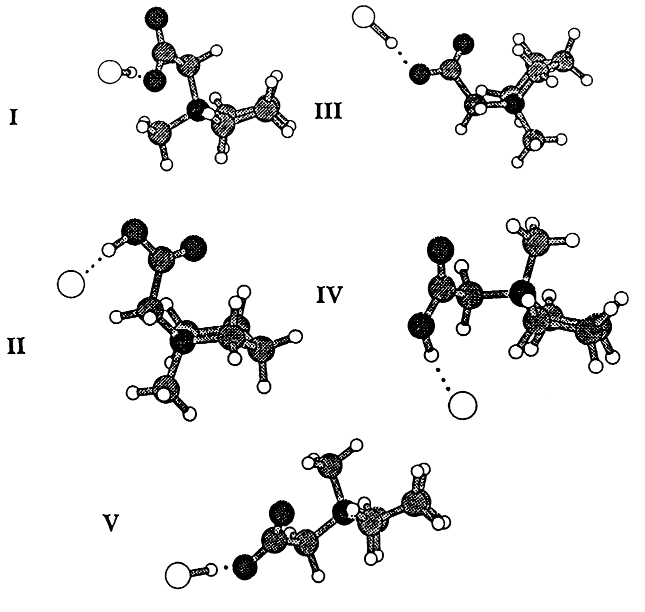

Fig. 3 MP2/6-31G(d,p) optimized structures of $C_4H_8N^+(CH_3)CH_2CO_2H{\cdot}Cl^-$

hydrochloride form simple hydrogen bonded complexes ($R_3N{\cdots}HCl$), without proton transfer in the gas phase,[51] even though they are stronger bases than MPRBET (pK_a = 1.92).

Conformer **II** is less stable than **IV** by 4.46 kcal mol^{-1} and 5.72 kcal mol^{-1}, respectively, at the BLYP and MP2 levels, whereas the remaining conformers differ by more than 9 kcal mol^{-1}. In conformers **I**, **III** and **V** the proton is closer to the chloride ion and the COO···H species has the more stable *syn* (*cis*) arrangement.[52] In more stable conformers (**IV** and **II**) the carboxylate group has an *anti* (*trans*) conformation. In formic acid the *anti* conformer is less stable than the *syn* conformer by 6 kcal mol^{-1}.[52] As Tables 3 and 5 show, when the N···Cl distance increases the relative energy also increases. The lowering of the attractive Coulombic interaction between nitrogen and chloride atoms is compensated by the interaction between the nitrogen and oxygen atoms.

Comparing the X-ray data with the calculations it seems that conformer **I** most closely resembles that in the crystal (Table 3), except for the H-bonded proton position.

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Techniques used: X-ray diffraction, MP2/6-31G(d,p) and BLYP/6-31G(d,p) calculations

References: 52

Tables 1–3, 6, 7: Crystal data, atomic coordinates, bond lengths, bond angles, torsion angles and thermal parameters

Fig. 1: Molecular structure and atom labelling of *N*-methylpyrrolidine betaine hydrochloride

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