Chemistry of Heterocyclic Compounds, Vol. 44, No. 10, 2008

STRUCTURE OF N-CHLOROMETHYLLACTAMS AND FEATURES OF THE INTERACTION OF ATOMS IN THEM AS A RESULT OF *ab initio* CALCULATIONS

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Quantum-chemical calculations have been carried out by the RHF/6-31G(d) and MP2/6-31+G(d) methods of molecules of N-chloromethylpyrrolidone, N-chloromethylcaprolactam, N-chloromethylsuccinimide, and N-chloromethylphthalimide with full optimization of their geometry, and also N-chloromethylpyrrolidone molecule by the RHF/6-31G(d) method at various angles of rotation of the CH_2Cl group around the C–N bond. It was shown that the lower frequencies of the ^{35}Cl NQR of the first two molecules in comparison with the later are mainly determined by the high populations of the p_σ-orbitals of their Cl atoms. The population of the orbitals of the unshared electron pair of the N atom is practically unchanged on rotating the CH_2Cl group, but the N atom polarizes the C–Cl bond in the indicated molecule. This does not confirm the supposed p,σ^*-conjugation in the Cl–C–N grouping.

Keywords: N-chloromethyllactams, population of *p*-orbitals, conformations of molecules, nonempirical quantum-chemical calculations, NQR parameters, p,σ^*-conjugation.

It is assumed (for example [1, 2]) that in the nonlinear triatomic grouping Y–C–M the unshared pair of electrons of the heteroatom M participates in p,σ^*-conjugation with the antibonding orbital of the C–Y bond, which leads to increased electron density on the indicator atom Y and to the properties of compounds containing such a grouping not corresponding to the inductive effect of M on Y. However it was shown (examples [3-5]) that the "anomalous" effect of M on Y, and the "anomalous" properties of such compounds caused by this, in reality corresponds to the polarization of the C–Y bond under the action of the charge on the M atom directly through the field.

Since the charge on the heteroatom M is not a point but is general, it is quite natural that the size of this "anomalous" effect of atom M on Y must depend on the position of the C–Y bond relative to the atom M. A significant contribution to the asymmetry of the electron distribution in atom M is introduced by its unshared pair of electrons. Consequently the size of the "anomalous" effect of M on Y must also depend on the mutual orientation of the C–Y bond and the unshared electron pair of atom M.

From a comparison of the experimental dipole moments and molar Kerr constants, and those calculated according to the additive scheme, the conformations of a large number of molecules containing the Cl–C–N grouping have been found, *viz.* N-chloromethylpyrrolidone [6], N-chloromethylcaprolactam [6], N-halomethylbenzamides $PhCONHCH_2Y$ where Y=Cl and Br [7], nitramine $ClCH_2NMeNO_2$ [8], etc. [9-11]. It is assumed that all three bonds of the nitrogen atom in these molecules lie in one plane, perpendicular to which is disposed

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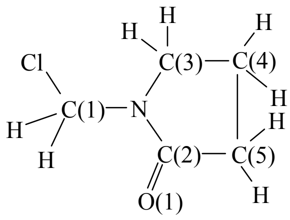
the 2*p*-orbital of its unshared electron pair. The angles (φ) estimated by these data, between this plane and that in which the N–C–Hal grouping is found (105, 90, 82, 95, and 102° respectively), are considered favorable of *p*,σ*-interactions (α effect), which must be maximal at φ = 90°.

To study the conformations of molecules containing the Cl–C–N grouping, and the mechanism of interaction of geminal atoms in it we, using the Gaussian 03W program [12], have carried out quantum-chemical calculations by the RHF/6-31G(d) and MP2/6-31+G(d) methods, of molecules of N-chloro-methylpyrrolidone (**1**), N-chloromethylcaprolactam (**2**), N-chloromethylsuccinimide (**3**), and N-chloromethyl-phthalimide (**4**) with full optimization of their geometry and also calculations by the RHF/6-31G(d) method of the molecule **1** at various angles of rotation (φ) of the chloromethyl group around the C–N bond (at φ = 0° the C–Cl and C=O bonds are in one plane in the *cis* position to one another).



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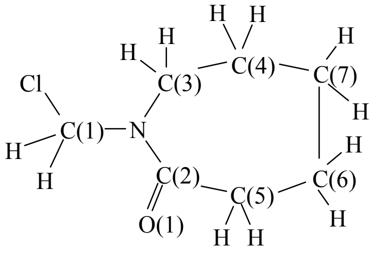

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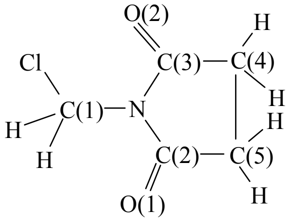

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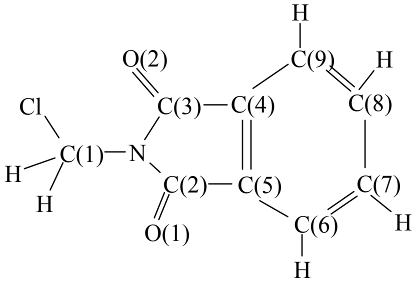

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The results of the calculations were compared with experimental data of the NQR method on ^{35}Cl nuclei. The frequencies of ^{35}Cl NQR (ν) and the parameters of asymmetry (η) of the electric field gradient on the ^{35}Cl nuclei were assessed according to equations (1) and (2) [13] and by the population of the less diffuse 3*p*-components of the valence *p*-orbitals of the chlorine atom, obtained in calculations of the molecules by the Hartree–Fock method using the splitted and polarized 6-31G(d) basis.

$$\nu = (e^2Qq_{\text{aт}}/2h[-N_z + (N_x + \mathrm{N}_y)/2](1+\eta^2/3)^{1/2} \qquad (1)$$

$$\eta = [3(N_x - N_y)/(2N_z - N_x - N_y)] \qquad (2)$$

Here e^2Qq_{at} is the atomic constant of quadrupole interaction, *h* is Planck's constant, N_x, N_y, and N_z are the populations of the valence p_x-, p_y-, and p_z-orbitals of the indicator atom respectively. The value of e^2Qq_{at} was found from the experimental NQR frequency of Cl_2 and the population of the 3*p*-components of the valence *p*-orbitals of the Cl atoms of this molecule calculated by the method indicated above.

Such a procedure for assessing the parameters of the NQR spectra, proposed by us previously (for example in [4, 14]), leads to a good agreement with the corresponding experimental data (for example [4, 14, 15]). The best agreement was reached when using populations of 3*p*-components obtained in calculations of the molecule by the RHF/6-31G(d) method [16].

TABLE 1. Bond Lengths (*d*) in the Molecules of **1-4**, Calculated by RHF/6-31G(d) and MP2/6-31+G(d) Methods

Bond	*d*, Å							
	RHF				MP2			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**
Cl–C(1)	1.817	1.824	1.794	1.798	1.810	1.819	1.789	1.795
C(1)–N	1.409	1.414	1.386	1.421	1.417	1.423	1.432	1.427
N–C(2)	1.368	1.379	1.386	1.395	1.382	1.391	1.402	1.411
N–C(3)	1.453	1.460	1.386	1.395	1.460	1.466	1.402	1.411
C(2)–O(1)	1.194	1.197	1.186	1.186	1.231	1.236	1.222	1.224
C(3)–C(4)	1.538	1.537	1.516	1.489	1.537	1.537	1.518	1.487
C(2)–C(5)	1.516	1.518	1.516	1.489	1.519	1.513	1.518	1.487
C(4)–C(5)	1.532	—	1.533	1.381	1.531	—	1.533	1.398

In the molecules of compounds **1-4** bond lengths were calculated with complete optimization of their geometry by the RHF/6-31G(d) and MP2/6-31+G(d) methods (Table 1) and also their valence and torsion angles (Table 2). As is seen the results of the calculations obtained by methods of different level are close to one another. According to both methods the three bonds of the N atom in the **1-4** molecules are practically in one plane, consequently the sum of its valence angles is almost no different from 360°.

For molecules **1** calculated by both methods the values of the angle φ practically agreed with those obtained previously [6], for molecule of **2** they differed from it comparatively insignificantly [6], but for molecules **3** and **4** the values agreed only in principle. According to the data of [17], both the latter molecules are planar ($\varphi = 0$ or 180°). However the planar conformation of these molecules is sterically less advantageous and was not commented on by the authors of [17], i. e. its results are probably erroneous.

It is assumed [6] that the planar conformation of the two latter molecules makes p,σ^*-conjugation in them impossible, while the conformation of molecules **1** and **2** is favorable to it, but the ^{35}Cl NQR frequencies of these compounds confirms the presence of such conjugation. Thus the NQR frequency for compound **1** (32.082 MHz) is significantly less than for MeCl (34.03 MHz), while for compound **4**, the planar structure of which excludes such conjugation, it is somewhat greater (34.367 MHz) [6]. However such a ratio of NQR frequencies of these compounds does not indicate any actual mechanism of interaction of atoms causing a reduction of NQR frequency of compound **1** in comparison with MeCl and compound **4**.

Certain conclusions on this mechanism may be drawn by comparing the experimental ^{35}Cl NQR parameters with the results of nonempirical quantum-chemical calculations of the corresponding molecules. The ^{35}Cl NQR frequencies, calculated by the method described above, of molecules **1** and **4** (Table 3) differ insignificantly from the experimental. Their small parameters of asymmetry are characteristic of Cl atoms bonded with an sp^3-hybridized carbon atom (regrettably the experimental parameters of asymmetry for these compounds are absent).

Judging by equation (1) and the population of $3p$-components of valence p-orbitals of Cl atoms in these molecules (Table 3), the lower ^{35}Cl NQR frequencies of molecules **1** and **2** in comparison with the same in molecules **3** and **4** are caused first of all by the higher populationsof $3p_z$ components of the valence p-orbitals of the Cl atoms in the first molecules. The significantly smaller contribution in its decrease introduces a somewhat lower partial sum of the populations of their $3p_x$- and $3p_y$-components. The total populations of the valence $p_z(p_\sigma)$-orbitals of Cl atoms in molecules **1** and **2** are also greater than in molecules **3** and **4** (Table 3).

In order to verify the ability of the unshared pair of electrons of the N atom (p_y-orbital) to participate in the interaction with the C–Cl bond in the studied molecules, we carried out calculations of molecule **1** by the RHF/6-31G(d) method at different angles of rotation (φ) of the ClCH$_2$ grouping around the C(1)–N bond and from the found population of $3p$-components of the valence p-orbitals of the Cl atom estimated the ^{35}Cl NQR

TABLE 2. Valence (α) and Torsion (β) Angles in Molecules **1-4**, Calculated by RHF/6-31G(d) and MP2/6-31+G(d)

Angle	RHF/6-31G(d)				MP2/6-31+G(d)			
	1	**2**	**3**	**4**	**1**	**2**	**3**	**4**
	α, deg							
ClC(1)N	112.7	113.8	112.3	112.7	112.3	113.6	111.8	112.3
C(1)NC(2)	122.2	118.2	123.0	123.6	122.3	117.9	123.2	123.5
C(1)NC(3)	123.5	119.4	123.0	123.6	123.8	119.3	123.2	123.5
C(2)NC(3)	114.3	121.6	114.0	112.5	113.9	121.1	113.6	112.2
NC(2)O(1)	125.3	121.8	124.4	125.2	125.2	121.8	124.3	125.0
NC(3)C(4)	103.2	114.6	107.9	105.4	102.6	113.8	107.7	105.4
NC(2)C(5)	107.3	116.2	107.9	105.4	106.8	115.5	107.7	105.4
C(3)C(4)C(5)	104.0	—	105.1	108.4	103.8	—	105.5	108.5
C(2)C(5)C(4)	104.2	—	105.1	108.4	103.8	—	105.5	108.5
	β, deg							
ClC(1)NC(2)	104.5	95.6	88.5	87.2	104.2	92.1	89.7	84.7
ClC(1)NC(3)	-73.9	-74.8	-88.5	-87.2	-74.2	-73.1	-89.7	-84.6
C(1)NC(2)O(1)	1.3	3.2	3.5	4.9	1.3	4.36	2.5	8.0
O(1)C(2)NC(3)	179.9	173.4	180.8	179.8	179.8	169.2	-178.1	178.4
C(1)NC(2)C(5)	179.5	-178.2	182.8	-175.8	179.5	-175.9	-178.1	-173.1
C(1)NC(3)C(4)	164.0	101.5	177.2	175.9	161.8	97.0	178.1	173.1
NC(2)C(5)C(4)	17.6	—	-0.1	0.6	19.9	—	-0.8	1.6
NC(3)C(4)C(5)	24.4	—	0.0	-0.6	27.9	—	0.7	–1.6

TABLE 3. Populations of the *p*-Orbitals of Cl Atoms ($\Sigma N_p = N_{3p} + N_{4p}$) and Their 3*p*-Components in Molecules **1-4**, Calculated by the RHF/6-31G(d) Method, Estimated according to the Population of 3*p*-Components of the ^{35}Cl NQR Frequencies (ν_{calc}) and Parameters of Asymmetry (η_{calc}) of the Electric Field Gradient on ^{35}Cl Nuclei

Molecule	Population	N_{p_x}, e	N_{p_y}, e	N_{p_z}, e	ν_{calc}, MHz	η_{calc}, %
1	N_{3p}	1.297	1.304	0.962	31.487	3.07
	ΣN_p	1.974	1.980	1.215		
2	N_{3p}	1.295	1.300	1.969	30.640	2.61
	ΣN_p	1.973	1.979	1.233		
3	N_{3p}	1.302	1.314	0.946	33.751	4.80
	ΣN_p	1.971	1.976	1.175		
4	N_{3p}	1.302	1.313	0.947	33.558	4.46
	ΣN_p	1.972	1.978	1.179		

frequencies (Table 4). For this the origin of the coordinates was placed at the nucleus of the Cl atom, the Z-axis was directed along the Cl–C bond. To assess the population of p_y-orbitals of the N atom the calculations were repeated placing the origin of the coordinates at the nucleus of the N atom.

According to the calculation performed, on increasing angle φ from 0 to 90° the ^{35} Cl NQR frequency was reduced. On further increasing angle φ it grew insignificantly and became closest to the experimental value at φ 125-130° (Table 4). Since in the crystalline state, for which the NQR spectra were recorded, the molecule is never found in the energetically most favorable form for the gas phase (for example, [18, 19]), it might be supposed that this angle φ is characteristic for molecule **1** in the crystal. In solution or in the gaseous state this molecule probably has angle φ ~105°.

According to ideas on *p*,σ*-conjugation between the unshared electron pair on the N atom and the antibonding orbital of the C–Cl bond in the Cl–C–N grouping, the least population of the p_y-orbital of the N atom (N_{py}) should be expected at φ 90°. However the results of calculations do not agree with this (Table 4). This population turned out to be lower at angles φ at which *p*,σ*-conjugation is not proposed.

TABLE 4. Calculated by the RHF/6-31G(d) Method at Various Dihedral Angles ClC(1)NC(2) (φ) the Partial Sum of the Populations of $3p_x$- and $3p_y$-Components ($\Sigma N_{3p/2}$) and the Populations of the $3p_z$-Components ($N3p_z$) of the Valence *p*-Orbitals of the Cl Atom, Estimated from Their ^{35}Cl NQR Frequencies ($\nu_{calc.}$), and also the Populations of the p_y-Orbital of the N Atom at the Sum of Its Valence Angles Σα (Np_y) and at 360° ($N'p_y$) in Molecule **1**

φ, deg	Cl			N		
	$\Sigma N_{3p/2}$, e	N_{3p_z}, e	ν_{calc}, MHz	Σα, deg	N_{p_y}, e	N'_{p_y}, e (360°)
0	1.319	0.925	36.665	—	—	1.750
30	1.314	0.933	35.412	359.1	1.742	1.750
45	1.307	0.948	33.509	355.2	1.700	-
65	1.302	0.959	31.960	355.3	1.700	1.743
90	1.300	0.963	31.363	359.0	1.729	1.735
104.5	1.300	0.962	31.487	360.0	1.734	1.734
120	1.302	0.960	31.827	—	—	—
125	1.302	0.959	31.961	—	—	—
130	1.303	0.958	32.105	357.9	1.708	1.735
150	1.306	0.955	32.658	354.2	1.672	1.738
180	1.310	0.950	33.489	352.5	1.664	1.740

Such a dependence of the population of the N atom p_y-orbital on angle φ is caused by the fact that the bonds of the N atom at various angles φ are not found in one plane. The sum of the valence angles of the N atom are somewhat less than 360° (Table 4), consequently the axis of symmetry of the N atom p_y-orbital does not coincide with the Y-axis of the system of coordinates, which shows up in the population of the N atom p_y-orbital.

In order to avoid this we carried out calculations of molecule **1** at various angles φ and fixed angles C(1)NC(2)O(1) and O(1)C(2)NC(3) (0° and 180° respectively), as a result of which the N atom is forced to preserve a planar configuration (the sum of its valence angles is equal to 360°). The populations of the N atom p_y-orbital ($N'p_y$) proved to be practically identical over a large range of changes of angle φ, including angles for which the proposed p,σ^*-conjugation must be maximal or generally impossible (Table 4). Consequently it is not obligatory to speak about transfer of the unshared pair of electrons of the N atom into the antibonding orbital of the C–Cl bond in this molecule. The N atom only polarizes the C–Cl bond directly through the field.

Probably the very same applies to other molecules containing Cl–C–M or Y–C–M groupings. In them the anomalous effect of the heteroatom M on the indicator atom Cl or Y is effected as a result of polarization of the Cl–C or Y–C bond under the action of the bulky charge of atom M directly through the field.

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