Nonempirical calculations of NQR spectrum parameters of azetidine

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The components of the ^{14}N electric field gradient (EFG) tensor, the corresponding nuclear quadrupole coupling constant (NQCC) χ, and the asymmetry parameter η of azetidine were calculated using the restricted Hartree—Fock—Roothaan method. The geometry of azetidine was optimized with the 4-31G basis set, and the values of the ring puckering angle (θ) and the angle between the N—H bond and the CNC plane (β) were refined with the 6-31G* basis set. The effect of choice of geometry on calculated NQR parameters was studied. To clarify the origin of EFG at the nitrogen atom nucleus, the contributions from individual bond orbitals and lone electron pairs to the EFG tensor components eq_{ii} were calculated in the framework of the LMO approach. It was demonstrated that the 4-31G + 6-31G*//6-31G* level calculations give NQCC and η values of azetidine that are in good agreement with the results of MW spectroscopy.

Key words: NQR, electric field gradient, *ab initio* calculations, LMO approach, geometry optimization.

Azetidine, as well as a number of other cyclic amines, has been studied[1] in the solid state by the NQR method. Based on results of this research, the nuclear quadrupole coupling constant (NQCC) χ and asymmetry parameter η have been determined:

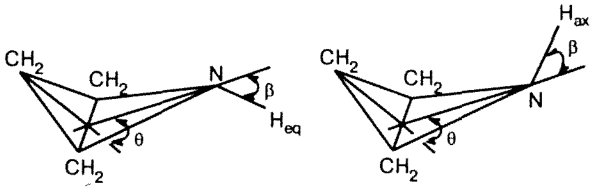
$$\chi = \frac{e^2 q_{zz} Q}{h},$$

$$\eta = \frac{eq_{xx} - eq_{yy}}{eq_{zz}}.$$

The principal components of an electric field gradient (EFG) tensor eq_{ii} can also be estimated theoretically with the help of a wave function, calculated in the framework of the *ab initio* Hartree—Fock—Roothaan method. Earlier[2,3] we have calculated χ and η for a number of three-membered heterocycles, in particular, aziridine and its derivatives, and analyzed the nature of EFG on the quadrupole ^{14}N nucleus in terms of local molecular orbitals (LMO). The calculation of NQR spectral parameters carried out in the present work for azetidine, the simplest representative of nitrogen-containing four-membered heterocycle, is a continuation of these studies.

Methods of calculations

According to the results of experimental studies carried out by different methods, the four-membered ring of azetidine is not flat but puckered. Below are estimates of the puckering angle in the azetidine cycle (θ) and its derivatives: 0° < θ < 14° from X-ray structural analysis[4], 15° < θ < 21° from NMR liquid phase data[5], $\theta \approx 30°$ according to the microwave spectroscopy (MW) method[6]. Thus, on going from the gas phase to a solid state the cycle flattens. Two conformations are possible depending on the orientation of the N—H bond relative to a puckered ring: equatorial and axial ones.



Based on the studies of azetidine and its derivatives by IR and Raman spectroscopy[7,8] a conclusion was made that both these conformations exist. However, more recent data, obtained by an electron diffraction (ED) method,[9] as well as theoretical studies[10,11] have led to the conclusion that azetidine has only one stable conformation, equatorial. It was established by RHF/6-31G** calculations[11] that there is no local minimum corresponding to the axial conformation on the potential energy surface of azetidine.

The inversions of the ring and the trivalent nitrogen atom in azetidine occur practically simultaneously, resulting in inversion of the molecule as a whole. The barrier to inversion in azetidine was estimated as ~6.5 kcal mol^{-1} with the 6-31G** basis (~6.46 kcal mol^{-1}, MP3[11]), *i.e.*, it is much less than in aziridine (19.2 kcal mol^{-1}) and agrees with the appropriate estimates for acyclic amines (3.8—7 kcal mol^{-1})[11], while an angular strain in the aziridine cycle substantially increases the

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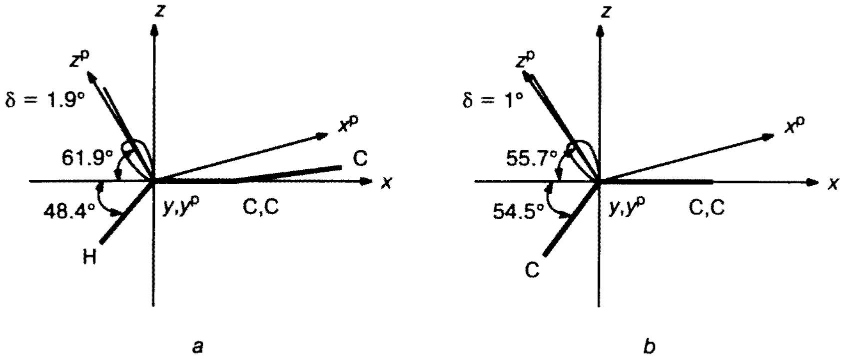

Fig. 1. Arrangement of principal axes of EFG tensor on ^{14}N in azetidine (*a*) and dimethylamine (*b*).

barrier. This fact, as well as approximate average values of pyramidal nitrogen atom angles (~107.6° in NH_3; ~108° in azetidine; ~94.8° in aziridine), also suggests[11] that the electronic density distributions in the vicinity of the nitrogen atom in azetidine and compounds of trivalent acyclic nitrogen are close to each other and differ significantly from the respective distribution in aziridine.

In this work the geometric parameters of azetidine were determined by optimization with the 4-31G basis with subsequent refining of angles θ and β to the minimum of the potential curve, calculated with the 6-31G* basis. The calculation was carried out for the conformation with equatorial orientation of the N—H bond relative to the plane of the ring (Fig. 1). The geometric parameters calculated by us and taken from the literature are presented in Table 1.

As seen from Table 1, the geometric parameters found by us are in good agreement with those calculated with the 6-31G** basis[11], except that of the CNC angle, which is underestimated in the 6-31G** basis compared to its experimental value. The θ angle calculated by us differs essentially from that found earlier[11] and from the experimental value measured for the molecule in the gas phase (ED + MW).[6,9] However, it is closer to the θ angle determined by the X-ray study (see Table 1). The geometric parameters of azetidine determined by us were used in the calculations of χ and η, and in the analysis of the nature of EFG on the nitrogen atom nucleus.

Table 1. The geometric parameters of the azetidine molecule (bond length in Å, angles in degrees), calculated by different methods

Parameter	4-31G + 6-31G*[a]	6-31G**[11]	ED + MW[6,9]	X-ray structural analysis[4]
R(N—C)	1.472	1.467	1.473	1.484
R(C—C)	1.553	1.540	1.564	1.548
R(C—H)	1.096	1.085(1.090)		
R(N—H)	0.994	0.999	1.014	
∠CNC	93.8	91.1	93.8	
∠CCC	87.5	85.7	84.6	
∠HCN	114.8	114.0	114.8	
θ	16.5	25.4	29.7	0—14
β	48.4	50.2	53.9	
E_{tot}(au)	−172.076266	−172.077008		

[a] Calculation scheme used in the present work (see text).

Results and Discussion

The calculated parameters of the NQR spectrum of azetidine are compared with the experimental data in Table 2. The orientation of the principal axes of the EFG tensor in the azetidine molecule determined from the 6-31G* basis calculations is shown in Fig. 1, *a*. The direction of the z^p axis is determined by the orientation of the lone electronic pair (LEP) of the nitrogen atom (deviation ~2°); the x^p axis is in a plane of the drawing, coinciding with the symmetry plane of the molecule; the y^p axis is directed out of the plane of the drawing.

As seen from Table 2, the calculated χ and η values are in satisfactory agreement with the experimental data for azetidine in the gas phase. Table 2 also shows that the empirically established proportionality between χ and η for five- and six-membered heterocycles[12] holds also in the azetidine case: $\chi_{NQR} < \chi_{MW}$; $\eta_{NQR} > \eta_{MW}$ ($\Delta \approx 0.15$ au). These are particularly the proportionalities which allow one to explain a more noticeable deviation for azetidine of the calculated χ and η from the values measured by the NQR method in the solid phase.

Earlier we emphasized the sensitivity of the calculated χ and η values to the geometric parameters used.[2] In this work we attempted also to estimate the influence of geometry on the results of NQCC and η calculations taking azetidine as an example. It was found that opening of the CNC angle causes an increase of eq_{yy} and eq_{zz}, resulting in an increase in χ and η (at Δ(∠CNC) ≈ 2° we

Table 2. Calculated and experimental χ and η values for azetidine[a]

Parameter	4-31G + 6-31G*//6-31G*[b]	Experiment gas phase (MW-spectr.)[6]	Experiment solid state (NQR)[1]
χ/MHz	−5.109	−4.44	4.358
η	0.100	0.157	0.303

[a] $\chi/\text{MHz} = eq_{zz}(\text{au}) \cdot Q/\mu_B \cdot 234.96$; $Q = 18.13\ \mu_B^2$.

[b] Geometry optimized with the 4-31G + 6-31G* basis; the NQR spectrum parameters are calculated with the 6-31G* basis.

found $\Delta\chi \approx 0.1$ MHz and $\Delta\eta \approx 0.025$). The same order variations of the calculated NQR parameters are also caused by an increase in angle β. The use of geometric parameters resulting from full optimization with the 6-31G** basis[11] for calculating χ and η gave $\chi = -4.848$ MHz, $\eta = 0.058$.

To improve further the quantitative agreement between calculated and experimental NQCC and η values it is apparently necessary to use a method which takes into account electron correlation, after preliminary optimization of the geometry of azetidine within the framework of the same method. Thus, for example, the results of NQCC χ calculation for pyridine[13] and pyrimidine[14] show that inclusion of electron correlation lowers the χ value by ~0.3 MHz as compared to that calculated by the SCF method.

As for comparison of the theoretical χ and η values with those measured by the NQR method, it is pertinent to notice the following. Since we were not able to find in the literature the complete structural data for azetidine in the solid phase, it is unknown how its geometry changes on going to the gas phase, and, hence, we cannot explain the discrepancy in the values of parameters obtained by different methods. One possible reason causing changes in the geometry and electronic structures of azetidine in the solid phase could be the formation of hydrogen bonds, which, as a rule, results in a decrease in χ and increase in η compared to their values in the gas phase. A similar explanation of the differences in NQCC and η values measured by the MW method and NQR spectroscopy is known, for example, for amines and a number of piperidine and pyrimidine complexes.[1] However, in the case of azetidine it can be considered only as an assumption not supported by special studies.

To clarify the nature of EFG on the azetidine ^{14}N nucleus the contributions to the eq_{ii} components from individual bonding orbitals and the LEP were calculated within the framework of the LMO approach. The results of calculation are presented in Table 3, from which it is seen that as in the case of nitrogen-containing three-membered cycles[2,3], the main contributions to the electron component of eq_{ii} come from the nitrogen atom LEP, two C—N, and N—H bonds. The summation of these contributions and account for the nuclear term give a rather accurate estimate of the eq_{ii} values. The eq_{ii} values for azetidine estimated in such a way (the nuclear terms are accounted for each contribution from the N—R bond orbital) are presented in Table 4; the differences between these estimates and calculated eq_{ii} values, taking into account the contributions from all bond orbitals in the molecule, are specified in the line «rest».

Table 3. Contributions from individual bond orbitals and LEP in EFG tensor components on ^{14}N in azetidine (au)

Contribution	eq_{xx}	eq_{yy}	eq_{zz}
Nuclear	0.447	0.125	−0.572
Electronic	0.092	0.535	−0.627
Total	0.540	0.660	−1.200
Core N	0.009	0.003	−0.012
LEP N	1.357	1.367	−2.724
2 C—N bonds	0.542	−1.759	1.217
Bond N—H	−1.640	1.058	0.583
2 C—C bonds	−0.120	0.053	0.067
6 C—H bonds	0.014	−0.106	0.087

Table 4. Main contributions in EFG tensor components on ^{14}N in azetidine and dimethylamine[a]

Contribution	Azetidine			Dimethylamine		
	eq_{xx}	eq_{yy}	eq_{zz}	eq_{xx}	eq_{yy}	eq_{zz}
LEP ^{14}N	1.357	1.367	−2.724	1.336	1.332	−2.667
N—H	−1.360	0.883	0.477	−1.447	0.915	0.532
2 N—C	0.551	−1.702	1.153	0.684	−1.762	1.080
Total	0.540	0.660	−1.200	0.540	0.630	−1.171[b]
«Rest»	0.007	0.113	0.106	−0.033	0.146	−0.115
η		0.100			0.077[b]	

[a] Contributions including nuclear terms. [b] Experiment: χ = 5.05 MHz, η = 0.2 (MW-spectroscopy)[15]; χ = 4.64 MHz, η = 0.325 (NQR)[1]; calculation: χ = 4.99 MHz[16].

As mentioned above, in the analysis of structural data for azetidine the assumption is put forward that the electronic distribution around the nitrogen atom nucleus of azetidine is closer to that of amines than to that of the higher strained three-membered cycles. Under this assumption we compared the contributions from the individual bond orbitals and LEP to the components of the ^{14}N EFG tensor in azetidine and dimethylamine (see Table 4). Such a comparison seems to be justified, since the differences in directions of the principal axes of the ^{14}N EFG tensor in these cases are small and equal to ~6° (see Fig. 1, *b*). The centroids of charge distribution in azetidine deviate from the C—N bond by ~6°. Thus, the angle between orbitals of C—N bonds is ~106°, and the corresponding angle in dimethylamine is ~112°.

The main contributions to eq_{ii} for dimethylamine are presented in Table 4, all of which are estimated in the same way as for azetidine (see Table 3). As the data in Table 4 show, the contributions to the eq_{ii} components from the LEP of nitrogen and its bonds with adjacent H, C atoms in azetidine and dimethylamine are similar. This confirms the above-mentioned assumption on the similarity of electronic distributions in the vicinity of the nitrogen atom nucleus in these molecules and explains the closeness of parameters of their NQR spectra. A similar analysis of the eq_{ii} contributions in aziridine demonstrated their essential difference from the corresponding values for dimethylamine.

The above data allow us to form conclusions on determining the role of peculiarities of bonding in the strained three-membered heterocycle on the parameters of NQR spectra.[3] The analysis of NQCC values for a series of $(CH_2)_nNH$ (n = 3—6) shows that weakening of the ring strain on going from aziridine (n = 3) to azetidine (n = 4) results in a growth of χ (from 3.58 MHz to 4.358 MHz[1]) and a reduction of η (from 0.525 to 0.303). Further increase of the heterocycle size up to five and sixmembers does not result in any appreciable change in the NQR spectra parameters as compared to azetidine: for pyrrolidine (n = 5) χ = 4.354 MHz, η = 0.344; for piperidine (n = 6) χ = 4.43 MHz, η = 0.310 [1].

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