Phase Transformation and Structure of N-chlorocarbonylisocyanide Dichloride*

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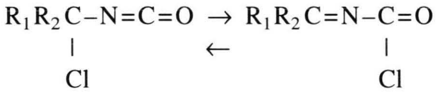
The ^{35}Cl nuclear quadrupole resonances in N-chlorocarbonylisocyanide dichloride show that it exists in two polymorphic forms. The metastable α phase has six ^{35}Cl NQR lines and the stable β phase has three. The latter is obtained irreversibly by annealing the α phase at 179 K. The temperature dependences of the ^{35}Cl NQR frequencies, spin-lattice and spin-spin relaxation times are obtained in both phases. The results of the ^{35}Cl NQR studies are discussed together with calculated MNDO level data and other physical properties (IR frequencies, dipole moments) of this compound.

Key words: N-Chlorocarbonylisocyanide Dichloride; Structure; Phase Transformation; ^{35}Cl NQR Parameters; MNDO calculation.

Introduction

α-Chloroalkylisocyanates, belonging to the heteroallylic class of compounds, present a good model of chlorotropic molecules [1] which exist frequently in equilibrium with the iminocarbonyl chloride form:



$$\underset{\mathrm{Cl}}{\underset{|}{\mathrm{R_1R_2C}}}{-}\mathrm{N{=}C{=}O} \;\underset{\leftarrow}{\rightarrow}\; \mathrm{R_1R_2C{=}N{-}}\underset{\mathrm{Cl}}{\underset{|}{\mathrm{C}}}{=}\mathrm{O}$$

According to IR [2] (solution) and dipole moment [3] (liquid) data the equilibrium for trichloromethylisocyanate is almost completely shifted towards the latter form – N-chlorocarbonylisocyanide dichloride (ICC). In the present communication we report on a ^{35}Cl NQR investigation of solid N-chlorocarbonylisocyanide dichloride together with MNDO calculations of stable and unstable (transitional state) isomers of this molecule.

Results and Discussion

ICC is liquid at room temperature. The metastable α phase is obtained by crystallizing ICC slowly at 194 K (the melting point). Six ^{35}Cl NQR lines of almost equal intensity and line width (~5 kHz) are observed (Table 1). The stable β phase is obtained irreversibly by one-hour annealing of the α phase at 179 K. During phase transformation the intensity of the α phase lines decreases steadily and finally vanishes. However, the group of lines at 32.843, 36.547 and 36.855 MHz fades out first. Herewith, three new signals of the β phase appear gradually. Thus, in the asymmetric unit cell of the α phase there are two crystallographically inequivalent molecule sites. Site (1) corresponds to the NQR lines that fade out first, while site (2) gives lines at 33.152, 36.714 and 38.404 MHz. It is necessary to mark that site (1) has low-

Table 1. ^{35}Cl NQR frequencies (ν), signal-to-noise ratio (*s/n*), spin-lattice (T_1) and spin-spin (T_2) relaxation times and average temperature coefficients (α_{av}) of N-chlorocarbonylisocyanide dichloride.

α Phase			
ν (s/n), MHz	T_1, ms	T_2, µs	α_{av}, kHz · K^{-1}
32.843 (5)	50	870	6.5
33.152 (6)	86	890	3.3
36.547 (10)	44	760	11.0
36.714 (11)	78	730	6.6
36.855 (10)	84	730	5.2
38.404 (13)	109	820	5.5
β Phase			
ν (s/n), MHz	T_1, ms	T_2, µs	α_{av}, kHz · K^{-1}
33.392 (14)	13	2200	5.2
37.091 (12)	55	680	5.2
38.277 (12)	75	620	4.4

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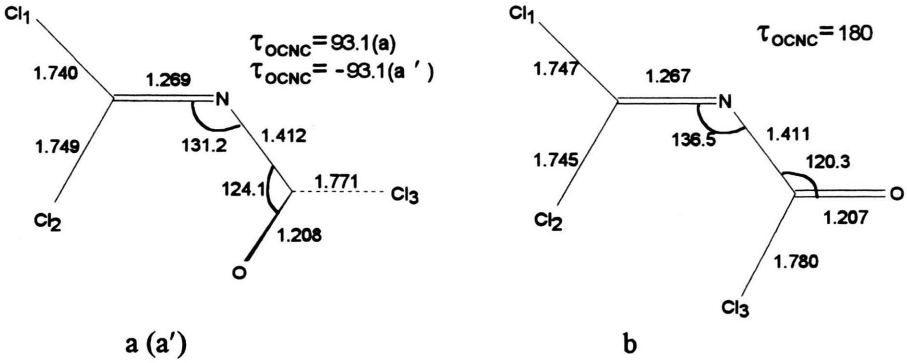

Fig. 1. *Gauche* (a), −*gauche* (a′) and *trans* (b) isomers of N-chlorocarbonylisocyanide dichloride. Bond distances are in Ångstroms, bond and torsion angles are in degrees.

Table 2. MNDO calculated total energy (E_{total}), heats of formation (ΔH_{f298}), dipole moment (μ), IR stretch vibration frequencies (νC=O, νC=N), atomic charges (q), and experimental ^{35}Cl NQR frequencies (77 K, β phase), IR frequencies [2] and dipole moment [3] of ICC.

Parameter	Transition state	±*Gauche* isomers	Experimental
E_{total}, hartree	−67.904	−67.911	–
ΔH_{f298}, kJ·mol^{-1}	−139.360	−157.870	–
μ, D	2.02	1.84	1.75
νC=O*, cm^{-1}	1800	1807	1790
νC=N, cm^{-1}	1645	1643	1650
q Cl$_1$, e	−0.024	−0.010	38.277 MHz
q Cl$_2$, e	−0.056	−0.067	37.091 MHz
q Cl$_3$, e	−0.156	−0.117	33.392 MHz

* Vibrational frequencies were scaled by 0.84 to account for the overestimation of them at this level of theory.

er T_1 values and higher temperature coefficients α_{av} than site (2), in agreement with the initial withering of the first group of frequencies. The values T_2 remain practically identical (within the error limits of the measurements) for both sites, noticeably increasing only for ClC=O group at the transition to the β phase.

For the determination of the conformational isomers at the sites of the α phase lattice, conventional molecular orbital calculations based on the MNDO scheme [4] were carried out. Optimized *gauche* (a) and −*gauche* (a′) isomers, together with the *trans* (b) isomer as the transitional state of the conformation transformation a → a′, are presented in Figure 1. The stable conformations a and a′ of ICC are not planar. The chlorocarbonyl group stands almost perpendicular to the $Cl_2C{=}N{-}C$ moiety plane, and the dihedral angle τ_{CONC} is ±93.1° for the ±*gauche* isomers, respectively. The activation energy E_a(a → a′) of the *gauche* to −*gauche* transformation is computed as 19 kJ · mol^{-1}, relative to that for the planar *trans* isomer (b) (see Table 2). Thus, in the α phase the ±*gauche* isomers of ICC can occupate inequivalent sites of the lattice. The mechanism of the $\alpha \rightarrow \beta$ phase transformation can be understood by using a model of strain relaxation and move of defects [5] as follows. In the metastable α phase, lattice strains and a number of possible lattice defects (for example, the mirror ±*gauche* isomers) develop. The strain relaxes by "annealing" (179 K), moving defects and averaging the electric field gradients. At the same time, the competition between the intramolecular and intermolecular forces is believed to be responsible for the phase transformation associated with the cooperative change of molecular conformation, i.e. torsion angle τ_{CONC}. In the new lattice of the β phase only one of the ±*gauche* isomers may probably exist. That explains the irreversibility of the phase transformation $\alpha \rightarrow \beta$.

We compare our theoretical results with available experimental parameters for ICC (Table 2). When analysing Table 2, one sees that good agreement between theory and experiment for the dipole moment and IR frequencies is obtained. The chemical non-equivalence of C-Cl bonds in the $Cl_2C{=}N-$ group is due to different O…Cl$_{1,2}$ interactions. The doublet-component NQR frequency spacing for the latter agrees with the difference of total charges on the chlorine atoms.

Experimental

ICC was prepared as described in [6]. ^{35}Cl NQR spectra were obtained by an ISSH 1-13M [7] pulsed spectrometer. Relaxation times were measured using a standard method [7] with 10% accuracy.

Conclusion

It may be concluded that the stable conformations of ICC are ±*gauche* isomers, where the chlorocarbonyl group stands almost perpendicular to the Cl_2 C=N–C moiety plane. The activation energy of the *gauche* to –*gauche* transformation was estimated by the MNDO method to be 19 kJ · mol^{-1}. The α phase of ICC contains possibly both ±*gauche* isomers in two crystallografically inequivalent lattice sites. The β phase comprises only one type of ±*gauche* isomers and can be obtained irreversibly by annealing the α phase at 179 K.

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