A SPECTROSCOPIC INVESTIGATION OF THE CONFORMATION EQUILIBRIUM OF CHLOROCYCLOHEXANE AND BROMOCYCLOHEXANE

Yu. A. Pentin, Z. Sharipov, G. G. Kotova, A. V. Kamernitskii, and A. A. Akhrem

M. V. Lomonosov Moscow State University
Translated from Zhurnal Struktumoi Khimii, Vol. 4, No. 2, pp. 194-200, March-April, 1963
Original article submitted September 13, 1961

We have studied the infrared absorption spectra and Raman spectra of $\text{C}_6\text{H}_{11}\text{Cl}$ and $\text{C}_6\text{H}_{11}\text{Br}$ in various aggregate states. We have determined the energy differences $\Delta E(a-e)$ of the rotational isomers of $\text{C}_6\text{H}_{11}\text{Cl}$ ($\Delta E_{\text{gas}} = 0.32 \pm 0.10$ kcal/mole and $\Delta E_{\text{liq}} = 0.28 \pm 0.10$ kcal/mole) and $\text{C}_6\text{H}_{11}\text{Br}$ ($\Delta E_{\text{liq}} = 0.25 \pm 0.10$ kcal/mole). Infrared spectroscopy has been used to study the polymorphic transformations of chlorocyclohexane and bromocyclohexane in the solid phase and their kinetics. We have made an experimental evaluation of the potential barrier for the conversion of the cyclohexane ring in these compounds and found it to be $V_0 \approx 15$ kcal/mole.

The cyclohexane ring can be represented in the forms of an "armchair" and "boat." Under ordinary conditions the concentration of molecules in the "boat" form is negligibly low, so that in structural investigations we are always dealing with the "armchair" form of the cyclohexane ring. Due to conversion of the ring, monoderivatives of cyclohexane exist in the form of two conformations $e$ and $a$ respectively with equatorial and axial arrangement of the substituent. Structural representations are also fairly well developed in the case of more complex derivatives of cyclohexane [1].

In cyclohexane and alkanes the $\overset{\text{C}}{\text{C}} \overset{\text{C}}{\text{C}}$ bond is characterized by staggered arrangement of the atoms immediately surrounding it; the conversion of the ring, like internal rotation in any alkane, is accompanied by the passage of these atoms through a "shaded" position, corresponding to the maximum of potential energy. The considerable difference in the conversion of the ring from internal rotation of the open molecule is that in the latter there can usually be complete circular rotation of the groups of atoms (through $360^\circ$), whereas in a ring this rotation can never take place without rupture. The ring conversion is therefore due to retarded internal twisting of the groups of atoms relative to each of the C–C bonds of the ring by only $\approx 120^\circ$. The potential curve of internal twisting (conversion) of cyclohexane in the form of an "armchair" can be represented by two minima and one maximum (Fig. 1a). In the case of monoderivatives of cyclohexane the $e$- and $a$-conformations existing in equilibrium can have different energies (Fig. 1b).

Our task was to conduct a spectroscopic investigation of conformation equilibrium of the two simplest derivatives of cyclohexane: the monochloro- and the monobromo-derivatives.

The Raman spectra of these compounds were studied by Kohlrausch [2] and the infrared absorption spectra were studied by Larnodie [3] and later by Klaeboe and co-workers [4], the latter work involving both the liquid and solid states. Kozlma and Sakashita recently used spectroscopic methods to study the conformation equilibrium of chlorocyclohexane [5]. These investigations revealed the presence of two stable conformations of $e$ and $a$ monoderivatives (Cl and Br) of cyclohexanes and a number of vibrational frequencies were reliably related to a given conformation; other information has been obtained in recent work. There is still not sufficient quantitative data on the conformation equilibrium of even such simplest derivatives of cyclohexane as $\text{C}_6\text{H}_{11}\text{Cl}$ and $\text{C}_6\text{H}_{11}\text{Br}$ and they are frequently contradictory. For example, practically all the existing data on this problem were examined in the review by Shepard [6]. We are unaware of any data on the size of the potential barrier of conversion (internal twisting) of the cyclohexane ring.

174
EXPERIMENTAL

The Raman spectra of liquid and solid substances were studied with the DFS-12 spectrometer (double monochromator with diffraction gratings and FEU-17 receiver) with excitation of the spectrum by the 4358 Å line from a low-pressure DRS-600 spiral mercury lamp. The method for obtaining the Raman spectra of frozen substances with thermostating was described earlier [7]. The spectral width of the slit varied between 7 and 15 cm⁻¹.

![Fig. 1. Quantitative potential curves of internal twisting (conversion). a) Cyclohexane; b) monoderivative of cyclohexane.](image)

The infrared absorption spectra of gaseous, liquid, and solid (in various modifications) substances were studied with the IKS-12 spectrometer with NaCl and KBr prisms. The vapors were thermostated in an ordinary gas cell with electrical heating, and thermostating of the liquids was in an ordinary sectional cell which had a metal jacket connected to a Wobser thermostat. The temperature was measured with a copper-constantan thermocouple. A special cell, described earlier [8], was used to obtain the spectra of frozen substances. The spectral width of the slit varied between 6 and 15 cm⁻¹ during the investigation of the infrared spectra.

During the recording of all spectra the rate of scanning was chosen so as not to affect the intensity of the bands.

The substances used as the objects of the investigation were synthesized and purified in the Institute of Organic Chemistry of the Academy of Sciences of the USSR; the constants of the compounds are given below:

- C₆H₁₁Cl, b. p. 44°C/21 mm, n²⁰ 1.4628
- C₆H₁₁Br, b. p. 54.5°C/15.5 mm, n²⁰ 1.4960

DISCUSSION OF RESULTS

The Raman spectra of liquid and crystalline chloro- and bromocyclohexane are given in Figs. 2 and 3, the frequencies of the peaks are shown in Table 1. The infrared absorption spectra of liquid and crystalline chlorocyclohexane are shown in Fig. 4, and the frequencies of the infrared absorption bands of chloro- and bromocyclohexane are also given in Table 1. The spectra which we obtained agree well with those previously published in the literature, but they are much more complete. However, we did not detect certain frequencies which had been mentioned previously as the lines of zero intensity (586 cm⁻¹ for C₆H₁₁Cl, 298 cm⁻¹ for C₆H₁₁Br, et al.).

It can readily be seen that when chloro- and bromocyclohexane are frozen their spectra change very strongly. In addition to the fact that the bands, as always on transition to the crystalline state, become narrower and are better resolved, there is also a considerable redistribution of the intensity in the spectra (see Figs. 2-4). In Raman spectra and infrared spectra of crystalline chlorocyclohexane the following frequencies disappear ("are frozen out"): 287, 475, 555 (563), 684, 808, 860, 868 and 1015 cm⁻¹ and for bromocyclohexane 368, 460, 680, 809, 868 and 1015 cm⁻¹. Furthermore, the intensity of a number of bands falls and the intensity of other bands increases, some bands becoming noticeable only in spectra of solids [796(792), 950 cm⁻¹]. The changes in the spectra of both substances are similar to the extent to which their structure is similar. For the molecules C₆H₁₁Cl and C₆H₁₁Br we related a number of vibrational frequencies—in particular, the "freezing out" bands of 684 and 660 cm⁻¹ respectively of chloro- and bromo-derivatives are related to the valence vibrations of C-halogen, and the frequency 808(809) cm⁻¹ is related to the pulsation vibrations of the ring of the a-conformation. The following frequencies are related to the vibrations of the