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CONFORMATIONAL ANALYSIS OF 2-CHLOROCYCLOHEXYLAMINE

Zen-ichi Yoshida

Department of Synthetic Chemistry, Kyoto University

Kyoto, Japan

Koji Nakagawa

Products Development Institute, Teijin Limited

Iwakuni, Japan

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2-Chlorocyclohexylamine may exist in two diastereoisomeric forms, one cis, the other trans. cis-2-Chlorocyclohexylamine and trans-2-chlorocyclohexylamine can be synthesized by the procedure in the literature. But conformational analysis of these compounds has not been reported. We determined the conformation of cis- and trans-2-chlorocyclohexylamine and their HCl-salts, spectroscopically.

cis-2-Chlorocyclohexylamine and its HCl-salt were obtained by the reaction of trans-2-aminocyclohexanol with PCl_5 in benzene (1). trans-2-Chlorocyclohexylamine and its HCl-salt were synthesized by the reaction of cyclohexenimine with dry HCl gas in ether (2). Infrared spectra of these compounds were measured on a Japan Spectroscopic Model DS-402G high resolution infrared spectrophotometer in the liquid state (for free amines) and crystalline state (for HCl-salts).

cis-2-Chlorocyclohexylamine has stretching vibration of C-Cl

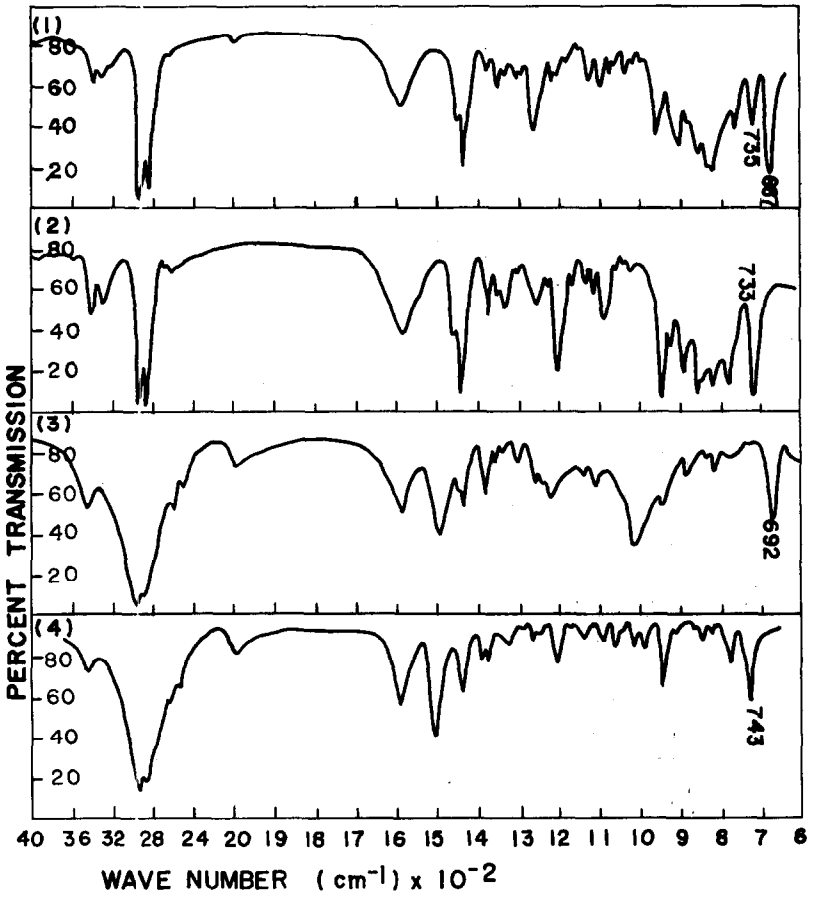

FIG. 1

Infrared absorption spectra

(1) cis-2-Chlorocyclohexylamin : pure liquid

(2) trans-2-Chlorocyclohexylamine : pure liquid

(3) cis-2-Chlorocyclohexylamine HCl-salt : KBr tablet

(4) trans-2-Chlorocyclohexylamine HCl-salt : KBr tablet

at 735 cm^{-1} and 687 cm^{-1}, while trans-2-chlorocyclohexylamine has one at 733 cm^{-1}. HCl-salt of cis-2-chlorocyclohexylamine has stretching vibration of C-Cl at 692 cm^{-1} and HCl-salt of trans-2--chlorocyclohexylamine at 743 cm^{-1}.

It is well known that equatorial substituents usually show typical infrared absorption at higher frequencies than axial substituents (3). For example, in chlorocyclohexane derivatives, infrared absorption band due to the equatorial C-Cl stretching is at 736-856 cm^{-1}, and that due to axial C-Cl stretching is 646-730 cm^{-1} (4). Therefore absorption bands at 735 cm^{-1}, 733 cm^{-1} were assigned to equatorial C-Cl stretching vibrations, while absorption bands at 687 cm^{-1} and 692 cm^{-1} were assigned to axial C-Cl stretching vibrations. From the results of above experiments, conformations of these compounds were determined as follows.

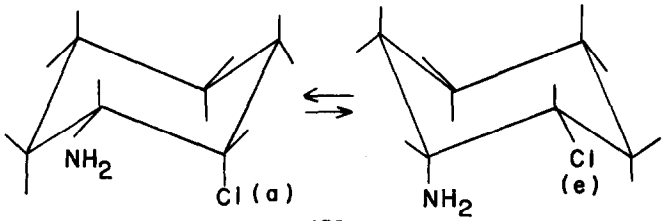

FIG. 2

Conformation of cis-2-chlorocyclohexylamine

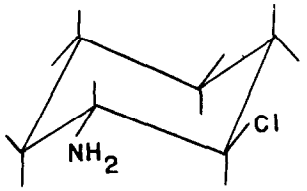

FIG. 3

Conformation of trans-2-chlorocyclohexylamine

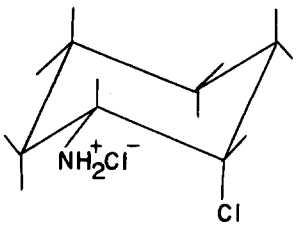

FIG. 4

Conformation of cis-2-chlorocyclohexylamine HCl-salt

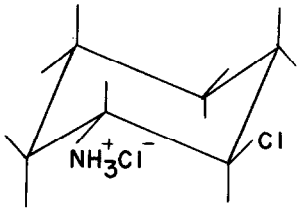

FIG. 5

Conformation of trans-2-chlorocyclohexylamine HCl-salt

References

1. G. E. Mclasland, R. K. Clark, Jr., and Herbert E. Carter, J. Am. Chem. Soc. 71, 637-42 (1949).

2. O. E. Paris and P. E. Fanta, J. Am. Chem. Soc. 74, 3007-3010 (1952).

3. E. L. Eliel, Stereochemistry of Carbon Compounds, p. 217 McGraw-Hill, New York (1962).

4. D. H. R. Barton, Experientia, Supple. II 121 (1955).