

Microwave, infrared, and Raman spectra, r_0 structural parameters, conformational stability and ab initio calculations of cyclohexylisocyanate



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ABSTRACT

The microwave spectrum of cyclohexylisocyanate, $c\text{-C}_6\text{H}_{11}\text{NCO}$, has been investigated from 10,000 to 21,000 MHz and 44 transitions for the more stable *equatorial-trans* conformer were assigned. The rotational constants of the ground vibrational state were determined: $A = 3546.87(28)$, $B = 936.12(1)$ and $C = 839.06(1)$ MHz. With these rotational constants and ab initio MP2(full)/6-311+G(d,p) predicted structural values, adjusted r_0 parameters for the *equatorial-trans* conformer were obtained. Variable temperature (-100 to -55 °C) studies of the infrared spectra (3500 to 400 cm^{-1}) of cyclohexylisocyanate dissolved in liquid xenon and the infrared spectra of the gas and solid were recorded. Additionally, the Raman spectrum (3600 to 100 cm^{-1}) of the liquid was investigated. Two conformers (*equatorial-trans* and *axial-trans*) were identified in the fluid states. An enthalpy difference of 397 ± 40 cm^{-1} (4.75 ± 0.47 kJ/mol) was obtained from seven conformer pairs with the *equatorial-trans* form more stable. Ab initio (MP2) calculations have been carried out by using a variety of basis sets.

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1. Introduction

The conformational analysis of cyclohexane and its derivatives have been of constant interest to molecular spectroscopists since the work of Hassel [1,2]. We began our investigation of six-membered rings with non-substituted cyclohexane by studying the relative intensities of the Raman active fundamentals and the potential function governing the conformational interchange between the *chair* and *twisted boat* form [3]. Since the *boat* form is so much higher in energy compared to the *chair* form, the amount of it present at ambient temperature is insignificant. To further understand the conformational stability of the *chair* form, studies were initiated to spectroscopically investigate monosubstituted chloro- [4], bromo- [5] and fluorocyclohexane [6] since there are only two conformers, *equatorial* and *axial* forms, which exist at ambient temperature. Due to the repulsive non-bonded nature of the interaction between the *axial* and the *equatorial* substituent, the *equatorial* conformation is generally favored [2,7] and these monosubstituted cyclohexanes exist predominantly in the

equatorial form. A significant number of studies have been carried out on the enthalpy differences for these halocyclohexanes by using vibrational spectroscopy and theoretical calculations such as infrared, Raman, nuclear magnetic resonance, and microwave spectroscopy. However, the enthalpy values varied over a wide range and for several cases the uncertainties were large i.e. 140 ± 105 cm^{-1} for fluorocyclohexane [6]. Additionally, several pseudohalogen substituted cyclohexanes i.e. cyanocyclohexane [8] and ethynylcyclohexane [9] have been studied and the lowest energy forms have been reported. However, the most stable conformation for cyanocyclohexane is an *axial* form [8,10] compared to the lowest energy *equatorial* form determined for all other substituted cyclohexanes in our investigations. Therefore, a study on another pseudohalogen, cyclohexylisocyanate, has been initiated to obtain additional information on the effect of the substituent on the ring. The molecule has a lot more conformational flexibility which is expected to provide an additional level of complexity to the conformational landscape of the conformation of six-membered ring molecules. Unlike the mono-halogenated and the linear polyatomic substitution, the isocyanate group has a higher degree of conformational flexibility due to the internal rotation angle of the isocyanate group. This angle makes it possible for more than one conformational minimum to exist.

There have been three studies [11–13] carried out on cyclohexylisocyanate that appeared to be inconclusive regarding its conformation, where especially lacking is any reliable data

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² Taken in part from the thesis of A.R. Conrad, which will be submitted in partial fulfillment for the Ph.D. degree.

regarding the relative position of the NCO moiety. The earliest one [11] was a nuclear magnetic resonance study where the investigators reported that the preferential conformation is the *equatorial* conformer with a predicted *equatorial:axial* ratio of $\sim 4:1$. A later vibrational study [12] was aimed to determine the conformational equilibria in the liquid state and in the crystal. The result of the study indicated that both the *axial* and *equatorial* form existed in the liquid phase as well as in solution. However, at low temperature cyclohexylisocyanate crystallizes in the *equatorial* form but when pressurized to 20 kbar at ambient temperature, the *axial* form is the preferred conformer. The third study [13] was carried out by utilizing low resolution microwave spectroscopy and seven transitions were assigned in the frequency range of 39–28 GHz. The author attempted to use the experimental $B+C$ value of 1702.9 ± 0.2 MHz to determine the most stable conformer by comparing it to the calculated $B+C$ values of the four possible conformers: *equatorial-trans* (*Eqt-t*), *equatorial-cis* (*Eqt-c*), *axial-trans* (*Axl-t*) and *axial-cis* (*Axl-c*). The $B+C$ values were calculated by using structural parameters from cyclohexyl fluoride [14,15] with the exception of the $\angle C_\alpha-N=C$, which is adopted from CH_3NCO [16]. The calculated $B+C$ value for *Eqt-c* form (1582 MHz) and *Eqt-t* form (1820 MHz) was the closest to the experimental value of 1703 MHz. The second part of the name refers to the orientation of the NCO moiety relative to the alpha H (Fig. 1). The structural adjustments needed to bring the experimental and calculated $B+C$ values into agreement would severely skew the conformation. The author [13] concluded that due to the low barrier to internal rotation, the molecule is freely rotating around the $C_\alpha-N$ bond and, therefore, the effective $B+C$ value does not correspond to any specific orientation of the NCO group. Although NCO substituted molecules tend to have a smaller barrier to internal rotation, it has been shown [17] that it is possible to determine decent rotational constants for molecules with similar low barrier.

As a continuation of our conformational analysis of cyclohexanes, extensive rotational and vibrational studies have been carried out on cyclohexylisocyanate. Variable temperature study of the infrared spectra has been recorded in liquid xenon and the relative stability of the *Eqt-t* and *Axl-t* conformer has been determined. In addition, r_0 structural parameters have been determined for the two most stable conformers by systematically adjusting the ab initio MP2(full)/6-311+G(d,p) optimized structure to fit the determined rotational constants obtained in this study. The results of these spectroscopic, structural and theoretical studies are reported herein.

2. Experiment and theoretical calculations

The cyclohexylisocyanate sample was purchased from Sigma Aldrich with a stated purity of 98%. The sample was further purified by using a low-temperature, low-pressure sublimation column

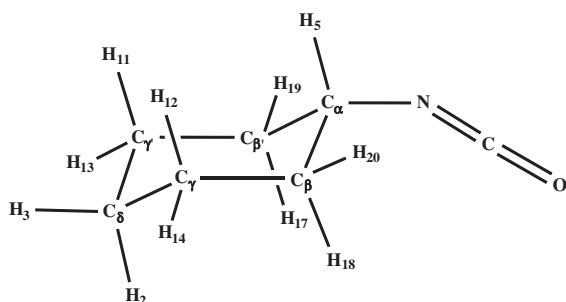


Fig. 1. Atomic numbering of cyclohexylisocyanate with the *equatorial* form shown. The relative orientation of the $-NCO$ moiety to the alpha H is indicated by the dihedral angle $\tau(C=N-C_\alpha-H_5)$: *Trans* ($\tau = 180^\circ$); *Cis* ($\tau = 0^\circ$).

and the purity of the sample was verified by infrared spectroscopic data. The sample was kept in the dark at low temperature until it was used.

The microwave spectra of cyclohexylisocyanate were recorded with a “mini-cavity” Fourier-transform microwave spectrometer [18,19] at Kent State University. The Fabry–Perot resonant cavity was established by two 7.5-inch diameter diamond-tip finished aluminum mirrors with a 30.5-cm spherical radius. The cyclohexylisocyanate sample was entrained in 70:30 Ne–He carrier gas mixture at 2 atm and expanded into the cavity with a reservoir nozzle [19] made from a modified Series-9 General Valve. The sample was irradiated by microwave radiation generated by an Agilent Technologies E8247C PSG CW synthesizer; details of the irradiation and its heterodyne detection circuitry can be found in Ref. [18]. Labview software controls the timing of the gas and irradiation pulses, as well as the detection of any free induction decay signal. The software performs signal averaging and can scan the spectrometer by stepping both the frequency source and the cavity. Microwave circuit elements allow for a spectral range from 10.5 to 26 GHz. The digital frequency resolution, governed by the sampling rate and the length of the free induction decay record, is 2.5 kHz. Rotational transitions are split into Doppler doublets centered at the transition frequency due to the coaxial orientation of the gas expansion to the cavity axis and the FWHM of each Doppler component is typically 13 kHz. The vacuum system can accommodate pulse repetition rates of up to 15 s^{-1} while maintaining a pressure below 10^{-4} torr, and the instrument can scan 450 MHz in 6 h while averaging 100 shots per scan segment. The frequencies for the measured transitions in the region of 12,000 to 19,000 MHz for the *Eqt-t* conformers of cyclohexylisocyanate are listed in Table 1 along with their assignments. Also listed are the frequency differences between the measured values and those obtained from the determined rotational constants and the centrifugal distortion constants (Table 2).

The mid-infrared spectra of the gas (Fig. 2) and solid (Fig. 3) were recorded from 3500 to 300 cm^{-1} on a Perkin–Elmer model 2000 Fourier transform spectrometer equipped with a nichrome wire source, Ge/CsI beamsplitter and DTGS detector. Atmospheric water vapor was removed from the spectrometer housing by purging with dry nitrogen. The spectrum of the gas was obtained with the samples contained in 12 cm cells equipped with CsI windows.

Table 1
Rotational transitional frequencies (MHz) for *equatorial-trans* cyclohexylisocyanate in the ground vibrational state.

Transition	ν (obs)	$\Delta\nu$	Transition	ν (obs)	$\Delta\nu$
6 _{1,6} – 5 _{1,5}	10339.34	–0.04	8 _{0,8} – 7 _{0,7}	13992.56	0.03
6 _{0,6} – 5 _{0,5}	10559.78	–0.08	8 _{2,7} – 7 _{2,6}	14167.46	–0.18
6 _{2,5} – 5 _{2,4}	10638.04	–0.19	8 _{4,5} – 7 _{4,4}	14216.62	0.17
6 _{4,2} – 5 _{4,1}	10657.65	0.03	8 _{4,4} – 7 _{4,3}	14216.62	–0.04
6 _{2,4} – 5 _{2,3}	10729.36	0.33	8 _{3,6} – 7 _{3,5}	14225.41	–0.10
9 _{0,9} – 8 _{1,7}	10887.87	0.03	8 _{3,5} – 7 _{3,4}	14236.72	–0.10
6 _{1,5} – 5 _{1,4}	10918.90	–0.30	8 _{2,6} – 7 _{2,5}	14376.01	0.44
2 _{2,0} – 1 _{1,0}	11486.50	–0.07	8 _{1,7} – 7 _{1,6}	14530.35	0.54
2 _{2,1} – 1 _{1,1}	11581.00	0.02	4 _{2,2} – 3 _{1,2}	14830.38	0.05
7 _{1,7} – 6 _{1,6}	12053.77	–0.01	4 _{2,3} – 3 _{1,3}	15372.83	–0.10
5 _{1,4} – 4 _{0,4}	12283.03	–0.28	9 _{1,9} – 8 _{1,8}	15471.99	0.10
7 _{0,7} – 6 _{0,6}	12283.03	–0.05	9 _{0,9} – 8 _{0,8}	15689.21	0.13
7 _{2,6} – 6 _{2,5}	12404.31	–0.18	9 _{2,8} – 8 _{2,7}	15927.12	–0.15
7 _{4,3} – 6 _{4,2}	12436.50	–0.01	9 _{4,5} – 8 _{4,4}	15998.07	–0.20
7 _{4,4} – 6 _{4,3}	12436.52	0.08	9 _{4,6} – 8 _{4,5}	15998.11	0.35
7 _{3,5} – 6 _{3,4}	12443.54	–0.10	9 _{3,7} – 8 _{3,6}	16008.18	–0.09
7 _{3,4} – 6 _{3,3}	12449.23	–0.09	9 _{3,6} – 8 _{3,5}	16028.80	–0.07
7 _{2,5} – 6 _{2,4}	12546.74	–0.29	9 _{2,7} – 8 _{2,6}	16212.96	–0.32
7 _{1,6} – 6 _{1,5}	12728.03	0.53	9 _{1,8} – 8 _{1,7}	16324.54	–0.29
3 _{2,1} – 2 _{1,1}	13175.20	0.17	5 _{2,3} – 4 _{1,3}	16463.12	0.11
3 _{2,2} – 2 _{1,2}	13452.95	0.00	7 _{1,6} – 6 _{0,6}	16547.34	0.29
8 _{1,8} – 7 _{1,7}	13764.69	0.03	5 _{2,4} – 4 _{1,4}	17340.90	–0.18

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