

Conformational Analysis of 1,1,2,2-Tetracyclohexylethane

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Abstract: A study of the title compound (**1**) has provided information on the way in which conformations and strain energies of 1,1,2,2-tetraalkylethanes change as a function of substituent size. As revealed by X-ray analysis and NMR studies, the ground-state conformation of **1** is gauche. Internal strain in **1** is indicated by abnormally wide Cy-C-Cy and Cy-C-C bond angles, by a long central C-C bond, and by the enthalpy of activation for thermolysis, which is intermediate between that of 2,3-dimethylbutane and tetra-*tert*-butylethane. The structure of **1** calculated by a combined empirical force field-extended Hückel MO method is in excellent accord with the results of the X-ray analysis. The marked divergence of the structure of **1** from the structures of tetracyclohexyldisilane and -diphosphine indicates that the steric demands of the cyclohexyl group find fuller expression in the more crowded ethane framework.

Recent work by Ingold and co-workers^{2,3} has indicated that 1,1,2,2-tetraalkylethanes prefer to adopt a gauche conformation. When the substituents are methyl groups, the compound (2,3-dimethylbutane) at room temperature consists of a nearly statistical (2:1) mixture of gauche and anti conformers.^{3,4} When the substituents are *tert*-butyls, only a single conformer is observed in solution,² whose structure, as calculated^{5,6} by the empirical force field (EFF) method, has C_2 symmetry, and has a H-C-C-H dihedral angle of ca. 100°, in agreement with observations (C_2 symmetry and $^3J_{\text{HH}} < 2$ Hz). A remarkable feature of this structure is the virtual eclipsing of the hydrogens with the quaternary *tert*-butyl carbons in a Newman projection of tetra-*tert*-butylethane.^{5,6} Small variations from perfect eclipsing (i.e., $\alpha = 0^\circ$ according to the notation of ref 6) lead to calculated $F_2\text{BFB}_2$ structures⁶ using the Allinger 1971⁷ ($\alpha = 3.6^\circ$) and 1973⁸ ($\alpha = 3.2^\circ$) force fields, to an almost perfectly eclipsed structure ($\alpha = 0.2^\circ$) using the Schleyer⁹ force field, and to calculated (FB)₃ structures⁶ using Allinger's 1977¹⁰ ($\alpha = -0.6^\circ$ ¹¹ or $\alpha = -4.1^\circ$ ¹²), Bartell's MUB-2¹³ ($\alpha = -11.5^\circ$), and White and Bovill's¹⁴ ($\alpha = -3.9^\circ$)¹⁵ force fields.

In 1,1,2,2-tetracyclohexylethane (**1**),¹⁶ the steric demands of the substituent cyclohexyl groups are expected to be intermediate between the two extremes of methyl and *tert*-butyl. One objective of the present study was to provide further information on the way in which ground-state conformations and strain energies of tetraalkylethanes¹⁷ change as a function of substituent size.¹⁸ The role of **1** as a missing link assumes particular significance in the context of a recently completed study¹⁹ of the static and dynamic stereochemistry of tetramethyl-, tetracyclohexyl-, and tetra-*tert*-butyldisilane and the corresponding diphosphines. A second goal of the present work was therefore a comparative conformational analysis of tetracyclohexyldisilane (**2**), -diphosphine (**3**), and -ethane (**1**). In addition, **1** is the last member in the series tetra-*tert*-butylethane^{5,6} and meso and racemic 1,2-di-*tert*-butyl-1,2-dicyclohexylethane (**4**),²⁰ whose structures and thermal stabilities have recently been investigated.

Methods and Results

Empirical Force Field Calculations. In our experience,²¹ the EFF method²² has proven highly effective in the calculation of ground-state structures of strained as well as unstrained hydrocarbons. As in the case of the stereochemically correspondent²³ molecule **2**,¹⁹ the conformational hypersurface of **1** is expected to be very complex, because the cyclohexyl group lacks a local axis of symmetry, i.e., each cyclohexyl ring may

in principle adopt one of three distinct (FB)₃ positions about the bond connecting it to the rest of the molecule. To perform EFF calculations on a molecule with such a complex potential energy surface a method must be found to limit the input structures to a reasonable number. Such a procedure has previously been outlined for **2**,¹⁹ and application of this algorithm to **1** yields a total of 9 C_2 gauche and 12 anti (three each of C_{2h} , C_i , C_s , and C_2 symmetry) input structures. Minimization of the 21 input structures by use of the Allinger 1971 force field (ALL)^{7,24} yielded 17 energy minima. The global minimum²⁵ (**1g**₁) was found to be gauche (C_2 symmetry) and to lie ca. 2 kcal/mol below the next most stable structure (**1g**₂), which is also C_2 gauche. Further structural details are provided in Figures 1 and 2. The most stable anti isomer (**1a**, C_i symmetry) was found to be only ca. 1 kcal/mol less stable than **1g**₂ (Table I). Because the three conformers are so close in energy, it seemed desirable to check the results by use of another force field. Accordingly, the 17 ALL minima were used as input structures for calculations²⁴ using the Schleyer force field (EAS).⁹ Minimization yielded a set of 17 new minima. The two sets of 17 minima were closely similar in structure; in particular, as shown in Figures 1 and 2, the characteristic structural features of the two lowest energy gauche forms (**1g**₁ and **1g**₂) calculated by EAS closely resemble the corresponding features calculated by ALL. However, although both force fields predict **1g**₁ to be the most stable conformer, EAS places **1a** slightly below **1g**₂ (Table I). This disturbing reversal in the relative order of calculated conformer stabilities prompted us to recalculate the energy of all 34 structures by the extended Hückel MO (EHMO) method. It had previously been shown²⁶ that in a number of instances the combined EFF-EHMO method leads to a reordering of relative energies, as compared to EFF calculations alone, and that the new ground states calculated by this hybrid method correspond to the experimentally observed structures. Application of the hybrid method to **1** led to a similar reordering of relative energies. As shown in Table I, using either of the two force fields, the EFF-EHMO method predicts a **1g**₂ ground state, although the relative order of **1g**₁ and **1a** remains force field dependent. In short, a clear-cut discrepancy exists in the predicted ground state: **1g**₁ by EFF alone (either ALL or EAS), vs. **1g**₂ by EFF-EHMO (either ALL or EAS). In light of the pronounced structural differences between **1g**₁ and **1g**₂ (Figures 1 and 2), the discrepancy was resolved by determining the X-ray structure of **1**.

X-ray Analysis. Crystals of **1**, obtained from *n*-hexane, were monoclinic, space group $P2_1/a$ with $a = 21.57$ (1) Å, $b = 11.379$ (5) Å, $c = 10.669$ (5) Å, $\beta = 119.74$ (5)°, and $d_{\text{calcd}} =$

Table I. Calculated Energies of Some 1,1,2,2-Tetracyclohexylethane (**1**) Conformers^a

structure	steric energy ^b		strain energy (25 °C)		rel energy			
	ALL ^d	EAS ^e	ALL	EAS	EFF		EFF-EHMO ^c	
					ALL	EAS	ALL-EHMO	EAS-EHMO
1g₁	25.23	41.79	18.03	22.83	0.00	0.00	4.33	3.01
1g₂	27.37	45.38	20.17	26.42	2.14	3.59	4.24	0.00 ^f
1a	28.11	44.94	20.91	25.98	2.88	3.15	5.02	2.15

^a In kcal/mol. ^b See Andose, J. D.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 2168, for a definition. ^c Structures calculated by the EFF method (ALL or EAS) and energies computed by EHT (see ref 26). All energies here are relative to a common value (EAS **1g₂**). ^d Refers to Allinger's 1971 force field. ^e Refers to the Schleyer force field. ^f The EHT total energy for this structure is -2641.8287 eV.

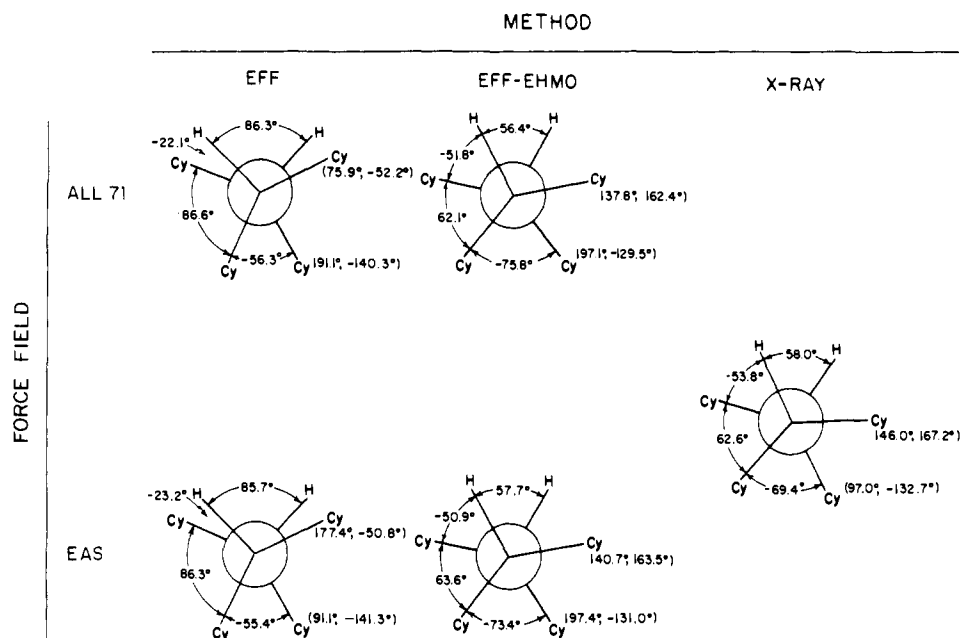


Figure 1. Structural details (Newman projections) for some conformations of 1,1,2,2-tetracyclohexylethane (**1**). Clockwise from the top left: Allinger 71 EFF ground state (**1g₁**); Allinger 71 EFF-EHMO ground state (**1g₂**); X-ray structure; Schleyer EFF-EHMO ground state (**1g₂**); Schleyer EFF ground state (**1g₁**). The numbers in parentheses give the two C_c-C_c-C-C dihedral angles (C_c = ethane carbon) for each cyclohexyl ring. The other numbers refer to the dihedral angles about the central bond. Each structure has C₂ symmetry, with the C₂ axis bisecting the C_c-C_c bond and the H-C_c-C_c-H angle.

1.048 g cm⁻³ for $Z = 4$ (C₂₆H₄₆, mol wt 358.7); $\mu = 3.6$ cm⁻¹.

The intensity data were measured on a STOE Weissenberg diffractometer (monochromatic Cu K α radiation, θ - 2θ scans); 3115 reflections $h01 \dots h71$ were measured for $2.5^\circ < \theta < 62.5^\circ$, of which 1584 with $I > 2.5\sigma(I)$ were used for structure determination and refinement. The data were not corrected for absorption.

The structure was solved by direct methods and was refined by full-matrix least squares.²⁷ In the final refinement anisotropic temperature factors were used for the carbon atoms and one common isotropic temperature factor for the hydrogen atom. The positions of the hydrogen atoms were refined in the last least-squares calculations. The final discrepancy values are $R = 0.068$ and $wR = 0.077$ for 1583 reflections. The final difference map has no peaks greater than ± 0.23 e Å⁻³.

A stereoview of the X-ray structure is provided in Figure 3. As shown in Figures 1 and 2 there is excellent overall agreement between the corresponding structural parameters (bond lengths, bond angles, and dihedral angles) of the X-ray structure and the ground-state structures calculated by the EFF-EHMO method (EFF = ALL or EAS), i.e., between the X-ray structure and **1g₂**.

Nuclear Magnetic Resonance Studies. No conformational information could be gained from ¹H NMR spectra. Even at 360 MHz, the spectrum in toluene-*d*₈ solution at 300 K showed only two broad and unstructured multiplets extending from

2.1 to 1.9 and from 1.6 to 1.3 ppm. The spectra at lower temperatures were similarly complex and did not allow individual signal assignments.

In contrast, variable-temperature ¹³C NMR spectra indicated the operation of a dynamic process, which is fast on the NMR time scale at 300 K and slow at 193 K. The temperature behavior of the spectra is fully consistent with a rotameric equilibrium between the three conformers with respect to the central ethane bond. ¹³C Chemical shifts at the extreme temperatures of measurement, along with a labeling scheme for **1**, are given in Table II. The assignments given are supported by proton undecoupled and off-resonance decoupled spectra. At 300 K only one set of signals was observed for the cyclohexyl rings, indicating fast exchange between the two different environments ("inner" and "outer") of the cyclohexyls in the gauche conformers. "Hidden partner" exchange²⁸ is indicated by the temperature dependence of the signal for the ethane carbons: on lowering the temperature, this signal broadens, reaching maximum broadening at 233 K, and then resharpens. This behavior is typical for "freezing out" an equilibrium between a major and minor component, whose signals cannot be observed because of severe broadening and low intensity.²⁸ The most reasonable assignment of the minor component is that of an anti rotamer. At 193 K only signals for the gauche conformer were observed. No individual assignments are possible for the signals of the two different cyclohexyl rings. Very probably, the signals for the β carbons at lower field belong to

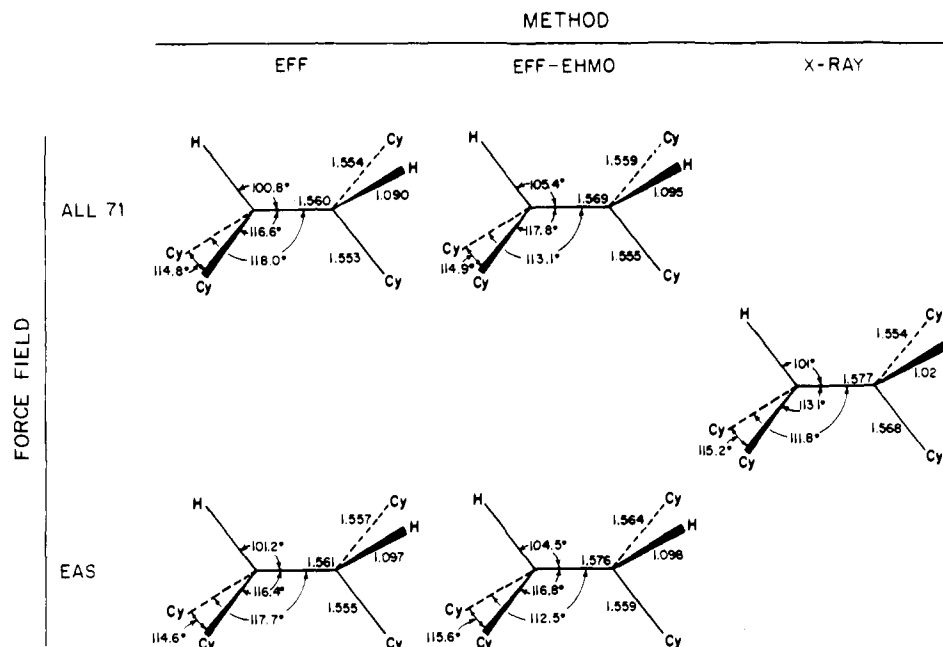


Figure 2. Structural details for some conformations of 1,1,2,2-tetracyclohexylethane (**1**). The structures are arranged as in Figure 1. The numbers on the right side of each structure are bond lengths (Å) and the numbers on the left are bond angles.

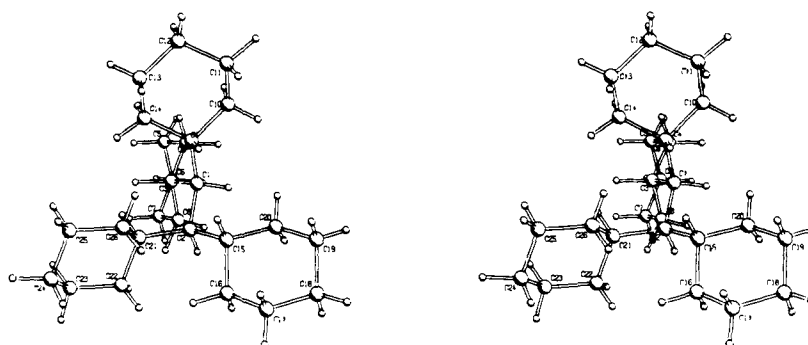


Figure 3. Stereoview of the X-ray structure of 1,1,2,2-tetracyclohexylethane (**1**).

the "inner" cyclohexyls, because these are sterically more crowded than the "outer" cyclohexyl rings.²⁹ No signals could be detected for the anti conformer. We estimate that under our conditions of signal-to-noise ratio, the presence of 10% of anti conformer should lead to detectable signals.

At 300 K, the gauche conformers are also the major components in the equilibrium mixture. This follows from an indirect determination of the vicinal coupling constant $^3J(\text{H}_c, \text{H}_e)$ between the equivalent ethane hydrogen atoms by a series of off-resonance decoupled ^{13}C spectra. No second-order features are observed in the doublet signal for C_c up to a reduction of the one-bond C_c, H_e coupling constant to about 5 Hz, leading to an upper limit of 3 Hz for $^3J(\text{H}_c, \text{H}_e)$.³⁰ These experiments also lead to an approximate determination of the proton chemical shift difference between the signals for H_c and H_e from the different reduced coupling constants for the corresponding ^{13}C signals. At 360 MHz, the chemical-shift difference is about 100 Hz.

Thermolysis Studies. The kinetics of the thermal decomposition of **1** in tetralin were followed by GLC as previously described⁵ at five temperatures between 368.6 and 398.8 K. The rate constants are recorded in Table III. From these data the following activation parameters were calculated: ΔG^\ddagger (300 °C) = 52.2 kcal/mol; ΔH^\ddagger = 62.9 ± 1.9 kcal/mol; ΔS^\ddagger = 18.4 ± 3.0 gibbs. From qualitative GLC analyses there was no indication of products other than those derived from the cleavage of the central $\text{C}_c\text{-C}_c$ bond.

Table II. ^{13}C Chemical Shifts of 1,1,2,2-Tetracyclohexylethane (**1**)^a

carbon atom	temperature		
	300 K ^b	300 K ^c	193 K ^c
C_c	48.94	49.54	49.64
C_{α}	39.22	39.75	40.12
$\text{C}_{\beta}, \text{C}_{\beta'}$	33.02	33.60	35.35
	32.59	33.14	35.28
$\text{C}_\gamma, \text{C}_{\gamma'}$	27.52	28.00	28.22
	27.30	27.78	27.62
C_δ	26.71	27.18	26.94

^a δ values in parts per million (±0.02 ppm), internal standard Me_4Si ($\delta_{\text{Me}_4\text{Si}}$ 0). ^b In $\text{CDCl}_3/\text{CCl}_4$ (1:2) at 45.3 MHz. ^c In toluene- d_8 at 90.5 MHz.

Discussion

The present study has shown that the conformation of **1** is gauche in solution (NMR studies) and in the solid state (X-ray analysis), and EFF calculations are in accord with these findings. In this respect, **1** exhibits behavior characteristic of

Table III. Rate Constants of Thermolysis of 1,1,2,2-Tetracyclohexylethane (**1**), 0.01 M in Tetralin

temp, °C	$10^4 k_1, s^{-1}$	$\pm 10^6 \sigma$	r	$\tau_{1/2}, h$
368.6	0.628	3.09	0.995	3.1
371.1	0.757	1.02	1.000	2.5
383.5	1.79	3.06	0.999	1.1
388.5	2.97	2.47	1.000	0.65
398.8	5.97	42.8	0.986	0.35

other 1,1,2,2-tetraalkylethanes.²⁻⁴ The Newman projections (Figure 1) of the X-ray structure and of the EFF-EHMO calculated ground state (**1g₂**) indicate almost perfect staggering of alternating bonds, from which it might superficially be concluded that **1** more closely resembles the relatively strainless 2,3-dimethylbutane than the highly strained tetra-*tert*-butylethane. However, the abnormally long central bond length (1.57 Å) and the exceptionally wide Cy-C-Cy and Cy-C-C bond angles (Figure 2) fit into the pattern set by the corresponding data for tetra-*tert*-butylethane and **4** and are unmistakable manifestations of internal strain, another measure of which is the thermal lability of **1**. It had previously been shown¹⁸ that a linear relationship exists between the thermal lability of substituted ethanes and their calculated strain energies, expressed by the equation

$$\Delta G^\ddagger(\text{kcal/mol}) = -0.60(\pm 0.03)E_s + 65.6(\pm 1.0) \text{ kcal/mol}$$

1,1,2,2-Tetramethyl- and tetra-*tert*-butylethane, and meso and racemic **4**, conform to this relationship, and the present work shows that **1** also fits it extremely well. For $E_s = 22.8$ kcal/mol (Table I) the calculated $\Delta G^\ddagger = 51.9$ kcal/mol is in excellent agreement with the experimental value ΔG^\ddagger (300 °C) = 52.2 kcal/mol.

A comparison of the structure of **1** with the structures of the corresponding disilane (**2**) and diphosphine (**3**) proves instructive. Whereas the structure of **1** is almost perfectly staggered with respect to the central C-C bond (Figure 1), both **2** and **3** are far from staggered, and possess one pair of nearly eclipsed cyclohexyl rings (cf. Figure 4 in ref 19). The remarkable similarity in the structures of **2** and **3**, and the equally remarkable contrast between these structures and that of **1**, supports the thesis that conformational preferences in such systems are primarily governed by metric rather than electronic properties.¹⁹ As might be expected, the divergence in the structures and stereochemical properties of these systems, i.e., 1,1,2,2-tetrasubstituted ethanes on the one hand, and disilanes and diphosphines on the other, increases with increasing steric requirements of the substituent groups.¹⁹ The marked difference between the structure of **1** and the structures of **2** and **3** is a manifestation of the appreciable steric demands of the cyclohexyl group, which find fuller expression in the more crowded ethane (as compared to disilane or diphosphine) framework.³¹

An additional and noteworthy result of the present study is the finding that the ground-state conformation of **1** was correctly predicted by EFF-EHMO²⁶ calculations, but not by unmodified, conventional EFF calculations alone. Although no attempt was made to calculate the structure of **1** by one of the several other available force fields, the principal conclusion seems inescapable: whenever EFF calculations reveal several minima on the potential hypersurface which are closely spaced in energy, considerable caution should be exercised in the selection of the global minimum, and recourse to experimental confirmation in these circumstances becomes highly desirable.

Experimental Section

NMR Measurements. ¹³C NMR spectra (45.3 MHz) were recorded

on a Bruker-Physik HX-180 spectrometer, and 90.5-MHz ¹³C and 360-MHz ¹H NMR spectra on a Bruker-Physik HX-360 spectrometer.

1,1,2,2-Tetracyclohexylethane (1). This compound was prepared by hydrogenating 1.5 g (4.2 mmol) of 1,1,2,2-tetraphenylethane in cyclohexane over 200 mg of Rh and 50 mg of Ru catalyst on Al₂O₃. The hydrogenation was performed in a high-pressure rocking autoclave at 200 °C and 300 atm of H₂. The ethane was isolated as an oil and crystallized from petroleum ether, mp 156–158 °C. Recrystallization from the same solvent yielded **1** (1.27 g, 79%), mp 157–158 °C (lit.¹⁶ mp 158–159 °C). The ¹H NMR spectrum featured resonances at δ_{CCl_4} (Me₄Si) 0.7–2.0 (m, alkyl H).

Anal. Calcd for C₂₆H₄₆: C, 87.07; H, 12.93. Found: C, 87.29; H, 12.86.

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Supplementary Material Available: Final positional and thermal parameters, standard deviations, a diagram with bond lengths and bond angles, and the observed and calculated structure factors of **1** (14 pages). Ordering information is given on any current masthead page.

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- (25) As used here, the term "global minimum" refers to the structure of lowest energy among those found on the potential energy hypersurface. Since practical considerations rule out a complete mapping of this surface in a complex system (e.g., **1**), the true global minimum cannot be unambiguously identified.
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(31) For example, the Cy-C-Cy angle of 115° found for **1** in the present work (Figure 2) is significantly larger than the Cy-Si-Cy angle of 112.4 (EFF calculation) or 112.0° (X-ray structure) found for **2**.¹⁹

Conformational Study of Cyclohexanecarboxaldehyde by Microwave Spectroscopy

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Abstract: The gas-phase microwave spectrum of cyclohexanecarboxaldehyde shows the presence of two stable conformational isomers. Both conformers have a chair cyclohexane ring with an equatorial aldehyde substituent, but differ in the value of the torsional angle about the C₁-CHO bond. Relative intensity measurements show that the gauche conformer (C=O eclipsing ring C₁-C₂) is more stable than the cis form (C=O eclipsing axial C₁-H) by 720 ± 200 cal/mol. A lower bound on the barrier height separating the two equivalent gauche forms has also been obtained.

Introduction

The stable conformations for CH₂XCOY compounds usually occur with the C=O bond eclipsing a C-H or a C-X bond,¹ although there are several known exceptions to this rule.² All these latter molecules exist in two conformations which both possess a plane of symmetry. Cyclopropanecarboxaldehyde³ and cyclopropanecarbonyl fluoride⁴ are also unusual since in each case two conformations exist with the carbonyl group cis or trans to the cyclopropane ring. The present investigation was undertaken to determine the conformations adopted by the six-membered cyclic ring compound, cyclohexanecarboxaldehyde (Figure 1). There is also some interest in comparing the results obtained here with a liquid-phase NMR study,⁵ and with a previous molecular mechanics calculation on this system.⁶

Experimental Section

The sample was obtained from the Aldrich Chemical Co. and was used without further purification. All spectra were taken on a Hewlett-Packard 8460 A microwave spectrometer. Useful intensities could only be obtained in R-band (26.5–40.0 GHz), with the sample cell cooled to ~-20 °C.

Results

Spectral Assignments. The low-resolution microwave spectrum revealed two distinct band series, arising from a-type, R-branch transitions of two separate conformers of cyclohexanecarboxaldehyde.⁷ The measured band spacing yielded two values for B + C which were both consistent with a chair cyclohexane ring with an equatorial aldehyde substituent. As expected, no band series corresponding to axial conformations were observed. To determine the C₁-CHO torsional angles corresponding to the observed conformations, a high-resolution microwave study was undertaken.

A sample of the high-resolution assignment for cyclohexanecarboxaldehyde presented in Tables I and II confirms that the observed conformations are cis (C=O eclipsing axial C₁-H) and gauche (C=O eclipsing ring C₁-C₂). The near prolate nature ($\kappa = -0.8$) for both species led to characteristic bunching of lines in the a-type, R-branch spectrum of the high K₋₁ transitions. Recognition of these patterns at low Stark modulation voltages considerably simplified the assignment process. Radio frequency-microwave double resonance was

also used to confirm initial assignments made under Stark modulation.⁸ The spectrum of the gauche conformer fit a simple rigid rotor model exceedingly well; the cis conformer, however, required the introduction of small centrifugal distortion constants to obtain a good fit (Table III).⁹ The spectrum of the gauche conformer also revealed the existence of two vibrational satellites, assumed to arise from successively excited states of the torsional mode about C₁-CHO. Relative intensity measurements give a fundamental vibrational spacing of 100 ± 40 cm⁻¹.

Structural Calculations. In the cis conformer, the aldehyde group lies in the plane of symmetry (a,c), and the quantity $P_{bb} = \frac{1}{2}(I_a + I_c - I_b) = \sum m_i b_i^2$ is independent of the aldehyde parameters. Following the procedure described for cyclohexyl fluoride by Pierce and Nelson,¹⁰ the ring angle C-C-C was adjusted to fit the observed value of P_{bb} . Good agreement with the cis rotational constants was then obtained by introducing the aldehyde substituent in the equatorial position with structural parameters assumed from acetaldehyde^{1a} (Table IV). Only small adjustments of the angles HC₁C and C₁CO (increase each by ~0.5°) were necessary to achieve an essentially exact fit.

A plot of the calculated rotational constants as a function of torsional angle about C₁-CHO, using the cis structural parameters, is shown in Figure 2. Comparison with the observed gauche rotational constants gives a dihedral angle of 117 ± 10°. The dispersion indicates that some other structural changes are occurring upon internal rotation.

Table I. Observed^a and Calculated Frequencies (MHz) for *cis*-Cyclohexanecarboxaldehyde

transition ^b	ν_{obsd}	$\Delta\nu^c$
$J'_{K'-1K'+1} - J''_{K''-1K''+1}$		
14 _{0,14} - 13 _{0,13}	31 392.50	0.00
14 _{1,14} - 13 _{1,13}	31 364.00	0.01
14 _{3,11} - 13 _{3,10}	35 251.19	0.06
14 ₈ - 13 ₈	33 982.84	-0.01
14 ₉ - 13 ₉	33 958.87	-0.02

^a Accurate to ±0.05 MHz. ^b Unresolved asymmetry doublets labeled by limiting prolate quantum number only. ^c Observed minus calculated frequencies from constants of Table III.