Mataga, *et al.*,[14] studied the hydrogen bonding of triethylamine with β-naphthol in benzene or *n*-heptane solvent by measuring the absorption and fluorescence spectra and found that the red shift (especially in benzene solvent) of the fluorescence spectra due to the hydrogen bonding is much larger than that of the absorption spectra, the shift of the latter being similar to that in this paper. To explain these phenomena they concluded that the ^1L_b equilibrium state of the β-naphthol would be mixed considerably with the charge-transfer state of the hydrogen-bonding system that is described as the charge transfer of one of the nitrogen atom's lone-pair electrons to the antibonding orbital of an O–H group. We can now expect that this mixing would modify the potential energy surface in the excited state considerably. In addition, strong hydrogen bonding reduces the molecular symmetry, so that more coupling among various vibrations becomes possible both in excited and ground states. The changes mentioned could bring about a broadening of the spectra of hydrogen-bonding species. Also, the fact that CH_2Cl_2 is a somewhat polar solvent may cause more broadening because of interactions with the proton donors and acceptors, as was discussed at the beginning of this section.

Finally consideration should be given to expected differences in the spectral shifts caused by hydrogen bonding in different electronic excited states. The electronic density, potential energy surface, and also the mixing with the CT state due to hydrogen bonding should be different in different excited states. So, in principle, the wave length shift due to hydrogen bonding should be different in other excited states. We can see from Table II that the red shift arising from hydrogen bonding with trimethylamine oxide or triethylamine at the D band of α-naphthol is larger than that observed for the bands A, B, and C, so that we can say that the band in question belongs to a different electronic state, namely the ^1L_a state; the same conclusion has also been reached by other authors.[9a,21]

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(21) In β-naphthol, on the other hand, band E (^1L_a)[9a] shows a smaller shift than for the A, B, C, and D bands (^1L_b state). The behavior mentioned above is quite similar to the substituent effect on the absorption spectra of naphthalene,[9] the same facts having been pointed out by previous workers.[9a,10]

Microwave Spectrum of Cyclohexyl Fluoride. Structure and Dipole Moment of the Equatorial Isomer

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Abstract: The microwave spectrum of cyclohexyl fluoride has been investigated in the frequency region 10 to 25 Gc. Twenty-six transitions are reported which can be attributed to rotational absorption by the equatorial form in its ground vibrational state. Rotational constants derived from the measured frequencies are $A = 4313.38$, $B = 2188.78$, and $C = 1591.61$ Mc. Assuming that the bonded CC and CH distances are the same in equatorial cyclohexyl fluoride as they are in propane, and that the ring structure is symmetrical, the following structural parameters are obtained: CF = 1.404, CC = 1.526, CH = 1.096 Å.; ∠CCC = 111° 22′, ∠HCH = 107° 34′, ∠HCF = 109° 13′, ∠CCF = 108° 39′, ∠CCH = 109° 29′; $\beta = 55° 2'$, where β = the dihedral angle for alternate CC bonds. Stark effect measurements yield $|\mu_a| = 2.08 \pm 0.03$, $|\mu_c| = 0.36 \pm 0.05$, and $\mu(\text{total}) = 2.11 \pm 0.03$ D. These data indicate that the dipole moment vector makes an angle of either 29° 40′ or 10° with the CF bond axis. In view of the fact that the CF bond moment is much larger than the CH bond moment, the angle 10° seems more probable than the angle 29° 40′.

Despite the interest and correspondingly vast literature concerning cyclohexane and its derivatives,[4] there have been no previous spectroscopic investigations of the structures of six-membered rings which are presumed to have both axial and equatorial isomers. The present work is concerned with the microwave spectrum of cyclohexyl fluoride and the structural and other information which it provides. Structures as determined from electron diffraction experiments have been reported for both cyclohexane[5] and cyclohexyl fluoride.[6] In the latter investigation, the ring structure of cyclohexyl fluoride (both forms) was assumed to be

(1) Alfred P. Sloan Foundation Research Fellow, 1961–1965.

(2) The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission.

(3) This is A.E.C. Document No. COO-38-442.

(4) See, for example, E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrisson, "Conformational Analysis," Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1965.

(5) M. Davis and O. Hassel, *Acta Chem. Scand.*, **17**, 1181 (1963).

(6) P. Andersen, *ibid.*, **16**, 2337 (1962).

the same as that of cyclohexane. With this assumption, analysis of the radial distribution curve clearly indicated that at ordinary temperatures there exist in the gas phase appreciable quantities of both axial and equatorial rotamers. Microwave spectroscopy provides the advantages that the two forms may be separately studied, and given that the spectra of a sufficient number of isotopic species are assigned, no assumptions need be made concerning the ring geometry in a determination of the structure.

While the rotational spectrum of only the common isotopic species of the equatorial form has been assigned in this work, reasonable assumptions, less stringent than those of ref. 6, can be made which allow a complete determination of the structure. It will be shown that the assumption of a common ring geometry for cyclohexane and cyclohexyl fluoride is indeed a very good approximation.

A value of 1.94 D. for the dipole moment of cyclohexyl fluoride as determined from dielectric constant measurements in benzene solutions has recently been published.[7] Stark effect measurements are reported here which provide inherently more detailed information concerning the electric dipole moment. Since the axial and equatorial forms exhibit individual rotational spectra, the effect on these spectra of an electric field provides the means for separate determinations of the dipole moments of the two forms. Moreover, these same measurements give some information concerning the orientation of the dipole moment vector.

Experimental Section

The sample of cyclohexyl fluoride, prepared by the addition of HF to cyclohexene, was kindly provided by Drs. E. L. Eliel and R. J. L. Martin. Over periods of the order of several hours, no evidence was found for decomposition of the sample in the waveguide absorption cell (brass, 1 in. × 0.5 in. × 15 ft.). Spectra were obtained with a spectrometer employing 100-Kc. Stark modulation (square wave), phase-sensitive detection, and oscilloscope display of absorption lines. Most of the measurements were made with the cell at room temperature. Some were made with the cell at the temperature of Dry Ice. The reported frequency measurements are believed to be accurate to 0.10 Mc. or better.

Microwave Spectrum

Both e- and a-$C_6H_{11}F$ have a plane of symmetry perpendicular to the intermediate axis of inertia, and thus both are expected to exhibit *a*-type as well as *c*-type rotational transitions. However, assuming that the dipole moment vector is approximately parallel to the C–F bond axis, and using reasonable structural parameters, calculations indicate that the rotational spectrum of the equatorial isomer should consist of strong *a*-type transitions and relatively weak *c*-type transitions, *i.e.*, $\mu_a >> \mu_c$. The reverse situation obtains for the axial isomer as calculations indicate $\mu_a << \mu_c$.

Five absorptions having a Stark effect characteristic[8] of $J = 3 \leftarrow J = 2$ R-branch transitions were found in the region 10–12 Gc. A detailed analysis shows these to be type-*a* transitions which are accounted for in the rigid rotor approximation by an entity having rotational constants *A*, *B*, and *C* of 4313.375, 2188.776, and 1591.605 Mc., respectively (see Table I). Attempts to find the corresponding type-*c* transitions resulted in failure, indicating that for this species $\mu_a >> \mu_c$, which as noted above is to be expected for the equatorial isomer.

Table I. Ground-State Rotational Transition Frequencies (Mc.) of Equatorial Cyclohexyl Fluoride

Transition	Frequency	
	Obsd.[a]	Calcd.[b]
$3_{03} \leftarrow 2_{02}$	10926.66	10926.70
$3_{13} \leftarrow 2_{12}$	10382.53	10382.43
$3_{12} \leftarrow 2_{11}$	12161.27	12161.22
$3_{22} \leftarrow 2_{21}$	11341.28	11341.14
$3_{21} \leftarrow 2_{20}$	11755.49	11755.59
$4_{04} \leftarrow 3_{03}$	14196.69	14196.66
$4_{14} \leftarrow 3_{13}$	13741.89	13741.84
$4_{13} \leftarrow 3_{12}$	16055.94	16055.93
$4_{23} \leftarrow 3_{22}$	15035.98	15035.93
$4_{22} \leftarrow 3_{21}$	15959.46	15959.56
$4_{32} \leftarrow 3_{31}$	15306.98	15306.87
$4_{31} \leftarrow 3_{30}$	15381.51	15381.46
$5_{05} \leftarrow 4_{04}$	17346.51	17346.63
$5_{15} \leftarrow 4_{14}$	17043.79	17043.80
$5_{14} \leftarrow 4_{13}$	19781.44	19781.43
$5_{24} \leftarrow 4_{23}$	18660.03	18660.06
$5_{23} \leftarrow 4_{22}$	20205.70	20205.67
$5_{33} \leftarrow 4_{32}$	19163.28	19163.24
$5_{32} \leftarrow 4_{31}$	19411.24	19411.36
$6_{06} \leftarrow 5_{05}$	20470.83	20470.86
$6_{16} \leftarrow 5_{15}$	20299.39	20299.33
$6_{15} \leftarrow 5_{14}$	23280.92	23280.97
$6_{25} \leftarrow 5_{24}$	22202.16	22202.25
$6_{24} \leftarrow 5_{23}$	24371.39	24371.33
$6_{34} \leftarrow 5_{33}$	22997.10	22997.03
$6_{33} \leftarrow 5_{32}$	23597.28	23597.36

[a] Estimated uncertainty, ± 0.10 Mc. [b] Calculated in the rigid rotor approximation using $A = 4313.375$, $B = 2188.776$, and $C = 1591.605$ Mc. The average deviation of observed and calculated frequencies is 0.07 Mc.

Thus we attribute these absorptions to rotational transitions of the equatorial isomer, noting in addition that the rotational constants derived from them are very nearly the same as those calculated using the structural parameters of e-$C_6H_{11}F$.[6] Table I lists the frequencies of 26 transitions of the equatorial isomer with *J* values ranging from 2 to 6. All are accounted for in the rigid rotor approximation with an average deviation of 0.07 Mc. and a maximum deviation of 0.14 Mc. A number of other transitions (Q-branches) with *J* values as high as 25 were also observed, but as they add nothing to the present discussion they are not reported. Attempts to assign the spectrum of the axial form have thus far been unsuccessful.

Stark Effect and Dipole Moment

Stark displacements of the $M = 0$ and 2 components of the $3_{03} \leftarrow 2_{02}$ transition and $M = 0$, 1, and 3 components of the $4_{04} \leftarrow 3_{03}$ transition were measured in order to determine the *a* and *c* components of the dipole moment. Stark coefficients are given in Table II. A least-squares analysis of these data yields $|\mu_a| = 2.08 \pm 0.03$ D., $|\mu_c| = 0.36 \pm 0.05$ D., and a total dipole moment of 2.11 ± 0.03 D. Since only the magnitudes of μ_a and μ_c are determined from these data, the orientation of the dipole moment vector is not uniquely determined. The data indicate that the angle between μ and the *a* axis (see Figure 1) is $9° 50' \pm 1° 30'$ with the sign of the angle undetermined. The structural calculations described in the next section indicate that the C–F bond axis makes an angle of

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(7) N. L. Allinger, M. A. DaRooge, and C. L. Neumann, *J. Org. Chem.*, 27, 1082 (1961).

(8) S. Golden and E. B. Wilson, Jr., *J. Chem. Phys.*, **16** 699 (1948).

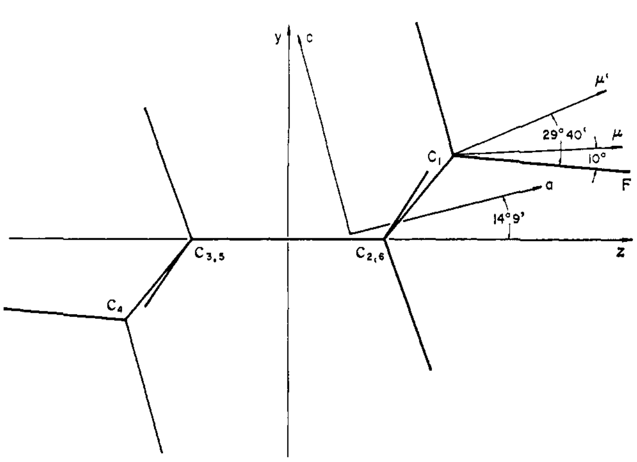

Figure 1. A planar projection of e-$C_6H_{11}F$ depicting relationships among various axes. The coordinates given in Table IV refer to the system of axes *x*, *y*, and *z*. Principal inertial axes are labeled *a*, *b*, and *c*, the origin coinciding with the center of mass of the molecule. The *x* and *b* axes are perpendicular to the plane of the page and are not depicted. The lines μ and μ' indicate the two possible orientations of the dipole moment. Arrowheads indicate what is assumed to be the negative end of the dipole.

19° 50' with the *a* axis, so that the two choices for the angle between μ and the C–F bond axis are 29° 40' and 10°, respectively. In view of the fact that the C–F bond moment is much larger than the C–H bond moment, the angle 10° seems more probable than does the angle 29° 40'.

Table II. Stark Coefficients and the Dipole Moment of Equatorial Cyclohexyl Fluoride[a]

		$\Delta\nu/E^2$, Mc./(kv./cm.)^2	
Transition	*M*	Obsd.	Calcd.
$3_{03} \leftarrow 2_{02}$	0	-6.45 ± 0.12	-6.35
	2	15.20 ± 0.30	15.53
$4_{04} \leftarrow 3_{03}$	0	-3.05 ± 0.06	-3.12
	1	-2.27 ± 0.05	-2.20
	3	5.24 ± 0.10	5.22
	$\lvert\mu_a\rvert = 2.08 \pm 0.03$ D.[b]		
	$\lvert\mu_c\rvert = 0.36 \pm 0.05$ D.[b]		
	μ(total) $= 2.11 \pm 0.03$ D.		

[a] Stark cell calibrated with OCS using μ(OCS) = 0.7124 D. [b] The subscripts *a* and *c* refer to principal inertial axes of e-$C_6H_{11}F$, which are approximately in the equatorial and axial directions, respectively (see Figure 1). The CF bond axis makes an angle of 19° 50' with the *a* axis while the dipole moment vector makes a corresponding angle of 9° 50' ± 1° 30'. Since the signs of μ_a and μ_c are not determined, there are two choices for the angle between the CF bond axis and the dipole moment vector. These are 29° 40' and 10°, with the latter being the more probable value.

Structural Calculations

The above data provide only the three moments of inertia of e-$C_6H_{11}F$ so that a number of assumptions or approximations are required in order to extract structural information. In this regard, it should be noted that irrespective of what assumptions are made, the problems of ring geometry and fluorine structural parameters are to a certain extent separable. Since the fluorine atom lies in the symmetry plane (*a,c*), the quantity $2P_{bb} = I_a + I_c - I_b = 2\Sigma m_i b_i^2$ is independent of the principal axis coordinates of the fluorine atom. Assuming that the ring has the same symmetry as that of cyclohexane, and that the CC and CH distances are the same as those of propane (1.526 and 1.096 Å., respectively),[9] P_{bb} depends only on the CCC and HCH angles. Assuming further that the sum of the HCH and CCC angles is twice the tetrahedral angle, as is required if the carbon atom bonding orbitals are sp hybrids[10], P_{bb} depends on a single variable which may arbitrarily be chosen as the CCC angle. A CCC angle of 111° 22' (see Table III) is required to fit the observed value of 101.93 a.m.u. Å.^{2} for P_{bb}. Changing the CCC angle by 1°, the CC distance by 0.01 Å., the HCH angle by 1°, and the CH distance by 0.01 Å. results in changes in P_{bb} of 1.5, 1.2, 0.14, and 0.20 a.m.u. Å.^{2}, respectively. Thus it is unlikely that the CCC angle as determined from P_{bb} in this manner is in error by more than 1°. Note that the ring geometry for e-$C_6H_{11}F$ as determined here is essentially the same as that reported for cyclohexane,[5] *i.e.*, ∠CCC = 111° 33' and CC = 1.528 Å.

Table III. Moments of Inertia (a.m.u. Å.^{2}) and the Structure of Equatorial Cyclohexyl Fluoride[a]

Ring geometry[b]			
		$I_a + I_c - I_b$	
∠CCC	β[c]	Calcd.	Obsd.
109° 28'	60°	198.6	
111° 22'	55° 2'	203.8	203.858
112° 24'	52° 0'	206.8	

Structural parameters[b]

CF = 1.404 Å.
CC = 1.526 Å.
CH = 1.096 Å.
∠CCC = 111° 22'
β = 55° 2'
∠HCH = 107° 34'
∠HCF = 109° 13'
∠CCF = 108° 39'
∠CCH = 109° 29'

	Moments of inertia	
	Obsd.	Calcd.
I_a	117.201	117.14
I_b	230.965	230.96
I_c	317.623	317.60

[a] $h/8\pi^2$ = 505531 Mc. amu. A.^{2}, m_H = 1.008142, m_C = 12.003804, m_F = 19.004456. [b] The quantity $I_a + I_c - I_b$ is independent of fluorine parameters and is used here to determine the ring geometry. The C–C and C–H distances are assumed to be the same as those of propane. For a given CCC angle the HCH angle is taken such that the sum of the angles is twice the tetrahedral value. [c] β = the dihedral angle for alternate C–C bonds.

Having used P_{bb} to fix the ring geometry, there remain two pieces of experimental data which may be used to determine the CF bond distance and the HCF angle. Choosing these parameters as 1.404 Å. and 109° 13', respectively, gives an essentially exact fit of P_{aa} and P_{cc}. Table III summarizes the structural calculations, and Table IV gives cartesian coordinates of the atoms in a convenient coordinate system (see Figure 1).

Distances, both bonded and nonbonded, obtained here compare very well with those obtained by electron diffraction; *e.g.*, C_1–F, C_2–F, C_3–F, and C_4–F distances

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(9) D. R. Lide, Jr., *J. Chem. Phys.*, 33, 1514 (1960).

(10) The requirement is a strict one only if the angles are very nearly tetrahedral. It is interesting that the experimental values for the CCC and HCH (methylene) angles of propane[9] very nearly satisfy this requirement. However, it must be noted that the argument which leads to this condition is approximate in that the effects of the orbital overlap (multicenter) are entirely neglected.

Table IV. Cartesian Coordinates (Å.) of the Atoms of Equatorial Cyclohexyl Fluoride[a]

Atom	x	y	z
C_1	0	0.6566	1.3190
H_1 (a)	0	1.7221	1.6026
F (e)	0	0.5174	2.7156
C_2	1.2604	0	0.7630
H_2 (a)	1.3262	−1.0313	1.1281
H_2 (e)	2.1432	0.5371	1.1281
C_3	1.2604	0	−0.7630
H_3 (a)	1.3262	1.0313	−1.1281
H_3 (e)	2.1432	−0.5371	−1.1281
C_4	0	−0.6566	−1.3190
H_4 (a)	0	−1.7221	−1.6026
H_4 (e)	0	−0.5793	−2.4123
C_5	−1.2604	0	−0.7630
H_5 (a)	−1.3262	1.0313	−1.1281
H_5 (e)	−2.1432	−0.5371	−1.1281
C_6	−1.2604	0	0.7630
H_6 (a)	−1.3262	−1.0313	1.1281
H_6 (e)	−2.1432	0.5371	1.1281

[a] The coordinates correspond to the structural parameters given in Table III. The axis system used is *not* the principal axis system. See Figure 1 which depicts the axes x, y, z and the principal axes a, b, c.

are reported[6] as 1.41, 2.35, 3.74, and 4.22 Å., respectively. The corresponding distances calculated from the coordinates given in Table IV are 1.404, 2.381, 3.736, and 4.202 Å. It is not surprising that the largest discrepancy occurs for the C_2–F distance. There are many other interatomic distances in both isomers in the range 2.1–2.6 Å. Thus this parameter is among the more difficult ones to obtain from an analysis of the radial distribution curve.

Discussion

It is interesting that the CCC angle in both cyclohexane and e-cyclohexyl fluoride is smaller than it is in propane by about 1°.[11] This fact can be rationalized by means of a relatively simple argument. In both cases, the equilibrium value of the CCC angle represents a compromise which minimizes the total strain energy resulting from valence angle and torsional deformations required for ring closure. For small deformations, the total strain energy may be taken as approximately proportional to

$$E = \frac{1}{2}K_\alpha(\alpha - \alpha_0)^2 + \frac{1}{2}K_\beta(\beta - \beta_0)^2 \tag{1}$$

where α is the CCC angle, β is the dihedral angle for alternate C–C bonds, and K_α and K_β are force constants. α_0 and β_0 represent the "strain-free" values of α and β. These angles are of course not independent, but are related by

$$\cos(\beta/2) = \sin(\alpha/2)/\sin\alpha \tag{2}$$

The appropriate value for α_0 is the CCC angle in propane (112.4°[9]). The choice of β_0 is rather more difficult to make. One obvious possibility is the corresponding dihedral angle in the *gauche* rotamer of *n*-butane. Unfortunately, this angle has not as yet been established with any great certainty. A more fundamental objection to this choice rests in the evidence[12] for a rather large H···H steric interaction. This interaction between the terminal methyl groups tends to make the dihedral angle larger than its "strain-free" value. Since the counterpart of this interaction in cyclohexane and its derivatives is a C–C bond, a direct comparison with *n*-butane is not possible. However, it seems plausible that when the effects of steric interaction are corrected for, the *n*-butane potential energy for internal rotation will approximate one which has threefold symmetry, in which case the *gauche* dihedral angle will be 60°; it is this value that we adopt for β_0.

For threefold or nearly threefold symmetry, the torsional potential energy has the approximate form $V(\beta) = {}^1/_2V_3(1 + \cos 3\beta)$, and K_β is ${}^9/_2V_3$. A barrier height of 3 kcal./mole corresponds to a value of 13.5 kcal./mole rad^2 for K_β. K_α has previously been estimated as 128 kcal./mole rad^2.[13]

Using the above parameters, eq. 1 is found to have its minimum for α = 111.1° and β = 55.8°. The corresponding experimental values are 111.4° and 55.0° for equatorial cyclohexyl fluoride, and 111.6 and 54.4° for cyclohexane. In view of the simplicity and approximate nature of this treatment, the agreement with experiment is surprisingly good. Note that the minimum of eq. 1 depends on only three parameters, K_α/K_β, α_0, and β_0. Of these the most uncertain parameter is β_0, so that the agreement might reasonably be interpreted as an indication that the "strain-free" dihedral angle in *gauche* *n*-butane is indeed very nearly 60°.

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(11) The present structural calculations for e-$C_6H_{11}F$ are "r_0" in nature and they depend heavily on the transfer of parameters from propane, in particular, the C–C distance. However, the C–C distance used here is a so-called "r_s" or substitution parameter. It might be argued, for the sake of consistency, that r_0 parameters of propane should be used here. Lide notes that the r_s parameters of propane give moments of inertia which are about 0.6% smaller than those observed. Stretching the r_s parameters by the factor 1.003 gives moments of inertia which are in essential agreement with those observed. This factor gives the C–C distance as 1.531 Å. Using this value rather than the r_s distance of 1.526 Å., the CCC angle of e-$C_6H_{11}F$ is found to be 111.0°. Thus, the $r_s - r_0$ ambiguity introduces an uncertainty of about 0.4° in the CCC angle. Note, however, that regardless of which C–C distance is used, the CCC angle found here is less than that of propane by about 1°.

(12) (a) K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940); (b) G. J. Szasz, N. Sheppard, and D. H. Rank, *ibid.*, **16**, 704 (1948); (c) R. A. Bonham and L. S. Bartell, *J. Am. Chem. Soc.*, **81**, 3491 (1959).

(13) J. B. Hendrickson, *ibid.*, **83**, 4537 (1961).