fying specific structural features suggested by a given approximate molecular wave function. For example, in selecting a wave function for naphthalene which gives the most favorable agreement between the calculated and experimental carbon-13 chemical shift values, one has a description of this molecule which predicts that the highest charge density (both σ and π) is at the β carbon. As the α position is more chemically reactive than the β, it is concluded that the free valency term, which is largest in the α position, dominates charge-density considerations in the chemistry of naphthalene. The σ and π charges obtained from the extended HMO treatment of phenanthrene failed to give the correct ordering of shifts at C-1 and C-2, and one can only hope that use of more refined treatments of this molecule will lead to the better agreement noted in the naphthalene case.

Summary

The relatively narrow range of values (-13.0 to $+5.5$) noted for the several aromatics studied in this work is in itself an unusual observation when one considers that the shifts in simple aliphatic hydrocarbons extend over a range of more than 50 ppm.[28] This emphasizes that the electronic environment of a carbon atom in various aromatic systems is remarkably similar and that variations are minor when compared to changes noted in other classes of compounds. Furthermore, the reasonable theoretical correlation of these small differences lends support to the accuracy of even simple wave mechanical treatments for these molecules. Recent inclusion of σ electrons into such theoretical treatments appears to result in even better agreement. The use of carbon-13 chemical shift data as a means of selecting between alternative approximate wave functions indicates that these data are superior to the corresponding proton values in ellucidating the details of the electronic structure of molecules.

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(28) D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.*, **86**, 2984 (1964).

Microwave Spectrum of Cyclohexyl Fluoride. Structure and Dipole Moment of the Axial Isomer, and the Axial–Equatorial Ratio

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Abstract: The microwave spectrum of axial cyclohexyl fluoride has been investigated in the frequency region 10 to 37 Gc/sec. Twenty-four absorption frequencies are reported which can be attributed to rotational transitions of a-$C_6H_{11}F$ in its ground vibrational state; rotational constants derived from the measured frequencies are $A = 3562.962$, $B = 2628.608$, $C = 1980.869$ Mc/sec. Assuming that the bonded CC and CH distances are the same in a-$C_6H_{11}F$ as they are in propane and that the ring structure has the same symmetry as cyclohexane, the following structural parameters are obtained: CF = 1.399, CC = 1.526, CH = 1.096 A, ∠CCC = 111° 42′, ∠HCH = 107° 21′, ∠HCF = 107° 51′, ∠CCF = 110° 0′, ∠CCH = 109° 24′, β = 54° 5′, where β = the dihedral angle for alternate CC bonds. Stark effect measurements yield $|\mu_a| = 1.05 \pm 0.02$, $|\mu_c| = 1.47 \pm 0.03$, and $\mu(\text{total}) = 1.81 \pm 0.03$ D. These data together with Stark effect measurements previously reported for the equatorial isomer establish that the dipole moment vector makes an angle of approximately 10° with the C_1F bond. (This vector lies between the C_1F and C_1H bond directions in both isomers.) Neither the difference in dipole moments of the two isomers (2.11 D. for e-$C_6H_{11}F$ and 1.81 D. for a-$C_6H_{11}F$) nor their orientations can be accounted for by the much used "bond moment" model. However, the "semiclassical" model of inductive effects proposed by Smith, Ree, Magee, and Eyring as applied to the present data is found to be in good agreement with experiment. This accord is not accidental as the same model is shown to account successfully for magnitudes and orientations of the dipole moments of several other fluoroalkanes. Comparison of the relative intensities of e-$C_6H_{11}F$ and a-$C_6H_{11}F$ rotational transitions indicate that the equatorial isomer is more stable than the axial isomer by 400 ± 300 cal/mole.

In a previous paper,[2] the results of an investigation of the rotational spectrum of the ground vibrational state of equatorial cyclohexyl fluoride were presented and analyzed for structural and dipole moment information. The present work is concerned with a parallel investigation of the microwave spectrum of the axial isomer. The experimental data not only provide the same kind of information concerning the axial form of the molecule, but when they are combined with data for the equatorial form additional information is obtained. Specifically, a comparison of Stark effect measurements allows the orientation of the dipole moment vector to be uniquely determined in both forms, and relative intensity measurements provide the means for estimating their energy difference.

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(1) The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is A.E.C. Document No. COO-38-494.

(2) L. Pierce and R. Nelson, *J. Am. Chem. Soc.*, **88**, 216 (1966).

Experimental Section

The sample of cyclohexyl fluoride, prepared by addition of HF to cyclohexene, was kindly provided by Drs. E. L. Eliel and R. J. L. Martin. The spectrometer used was of the Hughes–Wilson type[3] employing 100-kc (square-wave) modulation, phase-sensitive detection, and oscilloscope display of absorption lines. All of the measurements were made with the Stark cell at the temperature of Dry Ice. Frequency measurements reported here are believed to be accurate to ±0.03 Mc/sec or better. The accuracy of the oscillator on which all frequency measurements depended was monitored by phase comparison with the 60-kc signal of WWVB (call letters of an NBS radio station).

Microwave Spectrum

For any reasonable structural model of cyclohexyl fluoride, the intermediate axis (*b*) of inertia is found to be perpendicular to the plane of symmetry. Thus for both isomers *a*-type and *c*-type selection rules are operative. In the case of the equatorial isomer, only *a*-type transitions were observed because the dipole moment is very nearly parallel to the *a* axis (μ_a = 2.08, μ_c = 0.36 D.).[2] The rotational spectrum of the axial form is generally much weaker and more dense than that of the equatorial form for two reasons. The ground-state, axial–equatorial ratio is about $^1/_3$ at the temperature of Dry Ice, and the dipole moment is oriented such that *a*- and *c*-type transitions are of comparable intensity.

Table I lists the frequencies of 24 rotational transitions of a-$C_6H_{11}F$. The Stark effect provided the basis for assignment of all transitions. A least-squares analysis of these data in the rigid rotor approximation yields the following rotational constants: A = 3562.962, B = 2628.608, C = 1980.869 Mc/sec.

Table I. Ground-State Rotational Transitions of Axial Cyclohexyl Fluoride

Transition	Frequency, Mc/sec Obsd[a]	Frequency, Mc/sec Calcd[b]
$2_{11} \leftarrow 1_{01}$	11448.78	11448.79
$2_{21} \leftarrow 1_{11}$	13317.49	13317.49
$2_{20} \leftarrow 1_{10}$	12908.55	12908.52
$3_{12} \leftarrow 2_{11}$	14610.78	14610.75
$3_{21} \leftarrow 2_{20}$	14626.54	14626.52
$3_{12} \leftarrow 2_{02}$	17079.36	17079.35
$3_{22} \leftarrow 2_{12}$	18574.71	18574.71
$3_{21} \leftarrow 2_{11}$	17668.32	17668.35
$3_{31} \leftarrow 2_{21}$	20249.13	20249.17
$3_{30} \leftarrow 2_{20}$	20070.09	20070.07
$4_{04} \leftarrow 3_{03}$	16937.29	16937.33
$4_{14} \leftarrow 3_{13}$	16792.65	16792.63
$4_{13} \leftarrow 3_{12}$	19062.96	19063.00
$4_{23} \leftarrow 3_{22}$	18245.85	18245.83
$4_{22} \leftarrow 3_{21}$	19734.16	19734.16
$4_{32} \leftarrow 3_{31}$	18787.74	18787.70
$4_{31} \leftarrow 3_{30}$	19108.31	19108.29
$4_{13} \leftarrow 3_{03}$	23111.99	23112.01
$4_{23} \leftarrow 3_{13}$	24093.32	24093.34
$4_{22} \leftarrow 3_{12}$	22791.77	22791.77
$4_{32} \leftarrow 3_{22}$	25208.39	25208.44
$4_{31} \leftarrow 3_{21}$	24551.86	24551.85
$4_{41} \leftarrow 3_{31}$	27307.97	27307.93
$4_{40} \leftarrow 3_{30}$	27260.52	27260.50

[a] Estimated uncertainty ± 0.03 Mc/sec. [b] Calculated in the rigid rotor approximation using A = 3562.962, B = 2628.608, C = 1980.869 Mc/sec. Average deviation = 0.02 Mc/sec. Standard deviation = 0.03 Mc/sec. Standard errors of the rotational constants are less than 3 kc/sec.

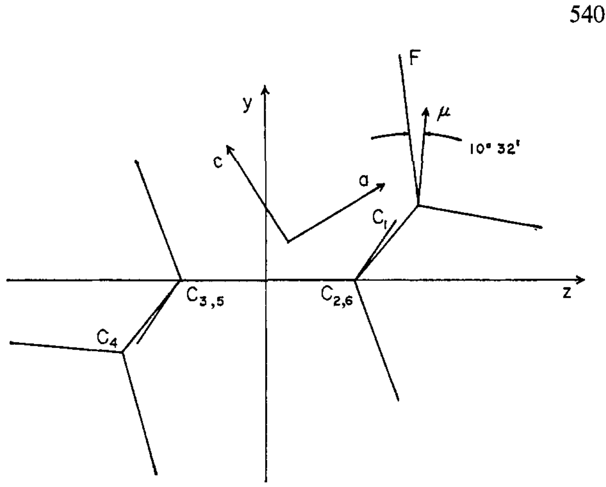

Figure 1. A planar projection of a-$C_6H_{11}F$ depicting relationships among various axes. Principal inertial axes are labeled *a*, *b*, *c*. The coordinates given in Table IV refer to the system of axes *x*, *y*, and *z*. The *x* and *b* axes are perpendicular to the plane of the page and are not depicted. The line labeled μ indicates the orientation of the dipole moment vector. The arrowhead indicates what is assumed to be the negative end of the dipole.

The average deviation of observed and calculated frequencies is 0.02 Mc/sec, and the standard deviation is 0.03 Mc/sec. Standard errors of the rotational constants are less than 3 kc/sec.

Stark Effect and Dipole Moment

Stark displacements of the M = 0 component of the $3_{12} \leftarrow 2_{02}$ transition, and the M = 1 and 2 components of the $3_{21} \leftarrow 2_{11}$ transition were measured in order to determine the dipole moment. Quadratic Stark coefficients are given in Table II. Theoretical coefficients were calculated according to the method of Golden and Wilson.[4] The data yield $|\mu_a|$ = 1.05 ± 0.02, $|\mu_c|$ = 1.47 ± 0.03, and a total dipole moment of 1.81 ± 0.03 D. Since the signs of the components are not determined, these data alone do not suffice to fix uniquely the orientation of the dipole moment vector. Thus, the angle between the *c* axis and the dipole moment vector is ±35° 34′ with an uncertainty of the order of 1°. From a structural analysis given in the next section, the CF bond axis is found to make an angle of 25° 2′ with the *c* axis, so that the two choices for the angle between the vector μ and the CF bond axis are 10° 32′ and 60° 36′ (see Figure 1).

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

Transition		$\Delta\nu/E^2$, (Mc/sec)/(kv/cm)^2 Obsd	$\Delta\nu/E^2$, (Mc/sec)/(kv/cm)^2 Calcd
$3_{12} \leftarrow 2_{02}$	$M = 0$	1.89 ± 0.05	1.91
$3_{21} \leftarrow 2_{11}$	$M = 1$	7.04 ± 0.07	7.07
	$M = 2$	35.0 ± 0.8	34.8
	$\lvert\mu_a\rvert$, D.	1.05 ± 0.02[b]	
	$\lvert\mu_c\rvert$, D.	1.47 ± 0.03[b]	
	μ, D.	1.81 ± 0.03	

[a] Stark cell calibrated with OCS using μ(OCS) = 0.7124 D. [b] The subscripts *a* and *c* refer to principal inertial axes of a-$C_6H_{11}F$ (see Figure 1).

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(3) K. B. McAfee, Jr., R. H. Hughes, and E. B. Wilson, Jr., *Rev. Sci. Instr.*, **20**, 821 (1949).

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

Stark effect data left a similar ambiguity for the equatorial form.[2] In that case the two possibilities for the angle between μ and the CF axis were found to be 29° 40′ and 10° 0′. Assuming that structural parameters for the two forms are essentially the same (see Table III for a comparison), then they are formally related to each other by a rotation by π of the H_1C_1F group about an axis lying in the $C_6C_1C_2$ plane and bisecting the $C_6C_1C_2$ angle. Assuming further that the dipole moments are similarly related, as for example would be required by a "bond moment" or a "group moment" model, then the combined Stark effect data clearly rule out the angle of 29° 40′ for the equatorial form and the angle of 60° 36′ for the axial form. Thus it is experimentally established on the basis of the above model that the dipole moment vector in both isomers lies between the C_1H and C_1F bond directions making an angle of about 10° with respect to the latter. In view of the fact that the electronegativity of fluorine is so much greater than that of carbon or hydrogen, there is virtually no uncertainty about the sign of $\vec{\mu}$, so that all ambiguities about the signs of μ_a and μ_c may be considered to have been removed.

Table III. Structural Parameters and Moments of Inertia (amu A^2) of e- and a-$C_6H_{11}F$[a]

Distance or angle	e-$C_6H_{11}F$[b]	a-$C_6H_{11}F$
CF, A	1.404	1.399
CC, A	(1.526)	(1.526)
CH, A	(1.096)	(1.096)
∠CCC	111° 22′	111° 42′
β[c]	55° 2′	54° 5′
∠HCH	(107° 34′)	(107° 21′)
∠HCF	109° 13′	107° 51′
∠CCF	108° 39′	110° 0′
∠CCH	109° 29′	109° 24′

	Obsd	Calcd	Obsd	Calcd
I_a	117.201	117.14	141.885	141.83
I_b	230.965	230.96	192.319	192.36
I_c	317.623	317.60	255.207	255.16

[a] $h/8\pi^2$ = 505531 Mc/sec amu A^2. m_H = 1.008142, m_C = 12.003804, m_F = 19.004456 amu. The CC and CH distances are assumed to be the same as those of propane. The quantity $I_a + I_c - I_b$ is independent of fluorine parameters and has been used to establish the ring geometry. [b] Taken from ref 2. [c] β = the dihedral angle for alternate C–C bonds.

In the next section evidence is given for a 400-cal/mole energy difference between the axial and equatorial forms with the latter being more stable. At room temperature this corresponds roughly to a 1:2 axial–equatorial ratio. Since the dipole moment of the equatorial isomer has been determined to be 2.11 D., the root-mean-square dipole moment at room temperature is calculated as 2.01 ± 0.03 D. This result compares quite favorably with the value of 1.94 D. as obtained by dielectric constant measurements on $C_6H_{11}F$ in solution with benzene.[5]

Relative Intensity Measurements and the Axial–Equatorial Ratio

Relative intensity measurements made at two or more temperatures provide the means for measuring the axial–equatorial ratio and their energy difference with a minimum of assumptions. Room and Dry Ice temperatures are particularly convenient. Unfortunately the spectra at room temperature, particularly of the axial form, are so weak that reliable measurements are difficult to obtain. Consequently, this information was sought from measurements made at a single temperature, that of Dry Ice. Apart from nuclear spin effects, the peak intensity of a rotational transition ($j \leftarrow i$) is proportional to

$$\frac{df_v}{T^{5/2}}(ABC)^{1/2}e^{-W_i/kT}(2J+1)|\mu_{ij}|^2\nu^2/\Delta\nu$$

where f_v is the fraction of molecules in the vibrational state v, W_i the rotational energy of the lower state, μ_{ij} the dipole moment matrix element, ν the resonant absorption frequency, $\Delta\nu$ the line-width parameter, and d the effective length of the absorption cell.[6] If it is assumed that $f_0(a) = f_0(e)e^{-\Delta\epsilon/kT}$ and that the line-width parameters are the same for the transitions whose relative intensities are measured, then all other quantities which determine the intensities are directly measurable or calculable, so that the measurement provides a value of $\Delta\epsilon = \epsilon_0(a) - \epsilon_0(e)$ – the energy difference of the axial and equatorial forms. The first assumption requires that the vibrational partition functions of the two isomers be identical. A complete vibrational assignment has not been made, and alternatives to this assumption are not readily apparent. With regard to the second assumption, no difference in line width was discerned experimentally. However, this measurement of $\Delta\nu$ is admittedly very crude.

The lines chosen for study were the $5_{15} \leftarrow 4_{14}$ transition of the equatorial form, and the $3_{21} \leftarrow 2_{02}$ transition of the axial form. Intensity measurements were made using the technique developed by Esbitt and Wilson,[6b] and they yield an energy difference of 400 ± 300 cal/mole with the equatorial form being the more stable. This result is more or less in accord with the ΔF value of 170 cal/mole obtained from electron-diffraction data[7] if it is assumed that ΔS is negligible. (Since the vibrational partition function has already been assumed to be the same, ΔS depends only on the rotational partition functions which differ for the two isomers by only 8%.) Nmr studies of cyclohexyl fluoride–tetramethylsilane solutions give ΔF as 250 cal/mole with the equatorial form predominating.[8]

Structural Calculations

In order to make comparisons as meaningful as possible, structural parameters have been calculated for a-$C_6H_{11}F$ subject to the same assumptions made in the case of e-$C_6H_{11}F$.[2] The quantity $2P_{bb} = I_a + I_c - I_b = 2\Sigma m_i b_i^2$ is independent of the coordinates of the fluorine atom since it lies in the a–c symmetry plane. Assuming that the ring has the same symmetry as that of cyclohexane and the CC and CH distances are the same as those of propane[9] (1.526 and 1.096 A, respectively), P_{bb} determines completely the ring geometry. The CCC angle required to fit the observed

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(5) N. L. Allinger, M. A. DaRooge, and C. L. Neumann, *J. Org. Chem.*, 27, 1082 (1962).

(6) (a) C. H. Townes and A. L. Shawlow, "Microwave Spectroscopy," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p 101; (b) A. S. Esbitt and E. B. Wilson, Jr., *Rev. Sci. Instr.*, 34, 901 (1963).

(7) P. Andersen, *Acta Chem. Scand.*, 16, 2337 (1962).

(8) A. Berlin and F. R. Jensen, *Chem. Ind.* (London), 988 (1960).

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

value of P_{bb} is 111° 42′ (20′ larger than that of the equatorial form). P_{aa} and P_{cc} serve to determine the remaining parameters which are 1.399 A for the CF distance and 107° 51′ for the HCF angle. The corresponding parameters of the equatorial form are 1.404 A and 109° 13′. Table III gives a complete comparison of all parameters of the two isomers. Table IV gives Cartesian coordinates of the atoms of a-$C_6H_{11}F$ in a convenient coordinate system. Andersen[7] has reported the following distances (in angstroms) obtained from electron diffraction measurements: $C_1F = 1.41$, $C_2F = 2.35$, $C_3F = 2.93$, $C_4F = 3.50$. The corresponding distances obtained in this work are 1.399, 2.397, 2.946, and 3.536 A.

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

Atom	x	y	z
C_1	0	0.6446	1.3272
F(a)	0	2.0076	1.0114
H_1(e)	0	0.5527	2.4194
C_2	1.2628	0	0.7630
H_2(e)	2.1414	0.5413	1.1280
H_2(a)	1.3409	−1.0305	1.1280
C_3	1.2628	0	−0.7630
H_3(e)	2.1414	−0.5413	−1.1280
H_3(a)	1.3409	1.0305	−1.1280
C_4	0	−0.6446	−1.3272
H_4(a)	0	−1.7150	−1.0915
H_4(e)	0	−0.5527	−2.4194
C_5	−1.2628	0	−0.7630
H_5(e)	−2.1414	−0.5413	−1.1280
H_5(a)	−1.3409	1.0305	−1.1280
C_6	−1.2628	0	0.7630
H_6(e)	−2.1414	0.5413	1.1280
H_6(a)	−1.3409	−1.0305	1.1280

[a] These coordinates are consistent with 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. A similar table in ref 2 erroneously gives the z coordinates of H_1(a) and H_4(a) respectively as + and −1.6026 A for the equatorial form. The correct values are + and −1.0626 A.

Discussion

The fact that the dipole moment of e-$C_6H_{11}F$ is 16% larger than that of a-$C_6H_{11}F$ cannot be rationalized by the simple "bond moment" model. In view of the fact that structural parameters are so nearly the same for the two isomers, this model requires that their dipole moments be essentially the same. A somewhat more sophisticated model based on a "semiclassical" treatment of inductive effects has been proposed by Smith, Ree, Magee, and Eyring.[10,11] The original application was made with reasonably good success to a number of simple C_1 and C_2 haloalkanes; *e.g.*, the model successfully accounts for the fact that dipole moments of CHX_3 molecules are appreciably less than those of their counterparts CH_3X. Applied to the case of cyclohexyl fluoride one obtains $\mu = 2.34$ D. for the equatorial form and 2.03 D. for the axial form. While the absolute values are too large by about 10%, the difference is in essentially complete agreement with experiment. Moreover, the calculated orientations are also in good agreement with experiment. The calculated angles (with respect to the CF bond) are 10° for the equatorial form and 16° for the axial form. These numbers are to be compared with the experimental values of 10° and 10° 32′, respectively.

Similar results are obtained for a number of other simple fluoroalkanes and are listed in Table V. In these calculations, the parameters of Smith, *et al.*,[10,11] have been used. They actually give three sets of parameters which differ according to assumptions made about the nature of the CH bond moment in methane. They demonstrated that particularly for the fluoroalkanes, results of the model are rather insensitive to both the sign and magnitude of the methane CH moment. For the sake of simplicity we chose to use those parameters corresponding to a CH moment of zero. Table V also compares the results of the "bond polarizability" model with those of the "bond moment" model in its simplest form.

Table V. Dipole Moments of Some Fluoroalkanes

	μ, D.			θ, deg		
Molecule	Obsd	BP[a]	BM[b]	Obsd[c]	BP[a]	BM[b]
CH_3F[d]	1.85	(1.81)	(1.81)	...	...	...
CH_2F_2[e]	1.96	1.89	2.12	...	...	...
CHF_3[f]	1.64	1.40	1.81	...	...	...
CH_3CH_2F[g]	1.96	2.05	1.81	7	12	0
CH_3CHF_2[h]	2.30	2.62	2.12	46	39	55
CH_3CF_3[i]	2.32	2.69	1.81	...	...	...
trans-$CH_3CH_2CH_2F$[j]	2.05	2.19	1.81	11	12	0
gauche-CH_3CH_2-CH_2F[j]	1.90	2.05	1.81	...	...	...
e-$C_6H_{11}F$[k]	2.11	2.34	1.81	10	10	0
a-$C_6H_{11}F$[l]	1.81	2.03	1.81	10	16	0

[a] Calculated using the "bond polarizability" model and parameters of ref 10. [b] Calculated using the "bond moment" model, and assuming tetrahedral angles. [c] Here θ is the angle between the dipole vector and the CF bond axis, except for CH_3CHF_2 where the angle is between the CC bond axis and the dipole vector. [d] D. M. Larkin and W. Gordy, *J. Chem. Phys.*, **38**, 2329 (1963). [e] D. R. Lide, Jr., *J. Am. Chem. Soc.*, **74**, 3548 (1952). [f] S. N. Ghosh, R. Tranbarulo, and W. Gordy, *J. Chem. Phys.*, **20**, 605 (1952). [g] B. Bak, S. Detoni, L. Hansen-Hygaard, J. T. Nielsen, and J. Rastrup-Andersen, *Spectrochim. Acta*, **16**, 376 (1960). [h] G. H. Kwei and D. R. Herschbach, *J. Chem. Phys.*, **32**, 1270 (1960). [i] R. G. Shulman, B. P. Dailey, and C. H. Townes, *Phys. Rev.*, **78**, 145 (1950). [j] Reference 13. [k] Reference 2. [l] This work.

In the present work the orientation of the dipole moment vector was experimentally determined *via* comparison of data on two isomers which are simply related by a rigid rotation of one part of the molecule (the HCF group) with respect to the other. Given an appreciable rotation of principal axes on isotopic substitution, Stark effect measurements on two or more isotopic species of the same molecule can and have been used to accomplish the same end. The results obtained here with the "bond polarizability" model as applied to cyclohexyl fluoride suggest that when neither of the above techniques is applicable, the model by itself may provide a reliable means for removing the sign ambiguities that are inherent in the analysis of Stark effect data.

An analysis of the accuracy of the structure determined here for a-$C_6H_{11}F$ and previously for e-$C_6H_{11}F$ is at best a difficult task. Many assumptions have been made and there are no isotopic checks of them. It is felt that rather pessimistic error estimates are ±1.5° for the CCC and HCF angles and ±0.015 A for the C_1F bond distance. In support of this we note that

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(10) R. P. Smith, T. Ree, J. L. Magee, and H. Eyring, *J. Am. Chem. Soc.*, 73, 2263 (1951).

(11) R. P. Smith and E. Mortensen, *ibid.*, 78, 3932 (1956).

the axial and equatorial C_1F distances as determined from the rotational constants differ by only 0.005 A, and that there is no good reason to expect that they should differ appreciably. Support for one of the more critical assumptions, that the CC bond length is the same as that of propane, is found in the electron-diffraction value[12] of the CC bond length in cyclohexane: 1.528 *vs.* 1.526 A as assumed here. Also noteworthy is that the CCC angle of cyclohexane determined by electron diffraction is 111° 33′[12] lying just between the spectroscopic values for e- and a-$C_6H_{11}F$. Finally, the stated errors are much more than adequate to account for any differences in the spectroscopic parameters and their electron-diffraction counterparts.

The relative accuracy of the results for the two isomers is quite another matter. Since the data for them has been treated in exactly the same way, errors in the differences of parameters to a large extent can be expected to cancel. Thus we believe that as the data indicate, the CCC angle is indeed slightly larger in the axial form, a result which is consistent with the notion that van der Waals repulsions between the axial fluorine atom and the axial hydrogens of carbon C_3 and C_5 may be appreciable. The indicated decrease of the HCF angle of more than 1° in going from the equatorial to the axial form is also consistent with this notion, as axial–axial repulsions might reasonably be expected to increase the corresponding interatomic distances. These same interactions should affect HCH and other angles as well, but the data are insufficient to evaluate these effects. In any event, the conclusions obtained here are relatively insensitive to assumptions about the HCH angle and CH parameters in general.[2]

It is of some interest to compare the present results with those from a microwave study of *n*-propyl fluoride by Hirota.[13] The equatorial form of $C_6H_{11}F$ is closely related to *trans*-propyl fluoride as the $FC_1C_2C_3$ and $FC_1C_6C_5$ chains are "*trans*-like." Similarly, these same chains are "*gauche*-like" in the axial form. On this basis alone it is not surprising that the dipole moment of the axial isomer was found to be 0.3 D. smaller than that of the equatorial isomer, as Hirota found the dipole moments of 2.05 and 1.90 D., respectively, for *trans* and *gauche n*-propyl fluoride.

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

(13) E. Hirota, *J. Chem. Phys.*, 37, 283 (1962).

Solvent Effects on the Fluorescence Spectra of Diazines. Dipole Moments in the (n,π^*) Excited States[1]

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Abstract: $n \leftarrow \pi^*$ fluorescence and excitation spectra as well as absorption spectra have been measured for pyridazine, pyrimidine, and pyrazine in isooctane, ether, acetonitrile, methanol, and water. The excitation spectra in the $n \rightarrow \pi^*$ transition region resemble the corresponding absorption spectra and are shifted to the blue with increasing polarity of solvents in the same way as the absorption spectra. The dipole moments in the (n,π^*) excited states are determined to be 1.1 D. for pyridazine and −0.5 D. for pyrimidine from the frequency shifts of absorption and fluorescence spectra in nonhydrogen-bonding solvents. The change of the dipole moments caused by the $n \rightarrow \pi^*$ promotion shows that significant reorganization is engendered in the Π distribution. In hydrogen-bonding solvents, a hydrogen bond formed between solute and solvent molecules gives rise to a large blue shift in the $n \rightarrow \pi^*$ absorption transition, but it has practically no effect upon the $n \leftarrow \pi^*$ fluorescence transition. It is concluded from these observations that the hydrogen bond is broken in the (n,π^*) singlet excited state.

In this paper two related questions are discussed: the dipole moments of the (n,π^*) singlet excited states in the diazines along with its concomitant implications to the excited-state charge distributions, and second the strength of the $N \cdots H$ hydrogen bond in the singlet excited states. The diazine excited-state dipole moments are of interest because of the activity in theoretical prediction of the properties of biological purines and pyrimidines. The dipole moment changes in going to the (n,π^*) excited state in the diazines should serve as stringent criteria for theoretical approaches and as key quantities in energy-transfer considerations.

With regard to the first question, the simplest interpretation of the $n \rightarrow \pi^*$ promotion is that one of the n electrons is transferred to the π^* molecular orbital which is completely delocalized over the entire ring. The transition should then be accompanied by a large decrease in the dipole moment.

An estimate of the decrease can be obtained by considering the change in dipole moment $(\Delta\mu)$ as being approximately equal to the moment of a dipole consisting of a unit positive charge located at the centroid of the nonbonding orbital and a unit negative charge at the center of the ring (*i.e.*, assuming for simplicity that the centroid of the π^* molecular orbital coincides

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