

In the  $C_5N_2$  species the N–N distance is 1.2 Å and the C–N distance is again 1.5 Å.

The representation of MO's of a molecule in terms of the MO's of independent fragments is a straightforward computation in the zero-differential overlap approximation. It should be noted that the MO's are determined for *isolated* fragments, but then translated so that the atomic orbitals in which the MO's are expressed are superimposed on corresponding AO's of the molecule in question. Under these conditions the expansion coefficients  $a_{ij}$  in the relation below are easy to evaluate. Here  $\phi_{M_i}$  is the  $i$ th MO of the

$$\phi_{M_i} = \sum_j \alpha_{ij} \psi_{F_j}$$

molecule and  $\psi_{F_j}$  is the  $j$ th MO of the set of fragments:

let  $\alpha_{M_i} = \sum_{\mu} C_{i\mu}^M \chi_{\mu}^M$  and  $\psi_{F_j} = \sum_{\nu} C_{j\nu}^F \chi_{\nu}^F$  where  $C$ 's are expansion coefficients and  $\chi_{\mu}$ 's are AO's; then

$$a_{ij} = \langle \phi_{M_i} | \psi_{F_j} \rangle = \sum_{\mu\nu} C_{i\mu}^M C_{j\nu}^F \langle \chi_{\mu}^M | \chi_{\nu}^F \rangle$$

Since  $\{\chi_{\mu}^M\} = \{\chi_{\nu}^F\}$  according to the argument above, and the zero-differential-overlap approximation is applied

$$a_{ij} = \sum_{\mu} C_{i\mu}^M C_{j\mu}^F$$

The values of  $a$  indicate to what extent a fragment MO is populated in the course of molecule formation.

A portion of the projection matrix  $a$  is reproduced in Table I, for the cyclobutene–methylene/bicyclo-[2.1.0]pentane system as corroboration of the schematic correlation diagram, Figure 5.

## Axial–Equatorial Energy Difference in Cyclohexyl Fluoride from Rotational Transition Intensity Measurements

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**Abstract:** Relative intensities of rotational transitions of the axial and equatorial conformers of cyclohexyl fluoride were measured to determine the energy difference of  $259 \pm 28$  cal/mol between the vibrational ground states. Partial power saturation of the transitions was used to increase the signal strength and to eliminate the dependence of the peak absorption coefficient on the transition line width. Differences in the rotational partition functions convert this energy difference to a free energy difference of  $298 \pm 28$  cal/mol at 187°K. Differences in the vibrational partition functions can only be approximated but should be such that this free energy difference is reduced by 50 cal/mol or less. Within the combined error limits, the gas-phase free-energy difference is the same as that determined in solution by nmr:  $276 \pm 15$  cal/mol from proton area ratio measurements in  $CS_2$ ,  $248 \pm 12$  cal/mol from fluorine area ratio measurements in  $CClF_3$ .

The equilibrium between the axial and equatorial conformers of cyclohexyl fluoride has been studied by electron diffraction,<sup>1</sup> nuclear magnetic resonance (nmr),<sup>2–5</sup> and microwave rotational spectroscopy.<sup>6,7</sup> For both conformers, the microwave study determined structural parameters and the magnitude and orientation of the dipole moment. Less definitive, however, was the value of  $400 \pm 300$  cal/mol found for the conformational energy difference from rotational transition intensity measurements. The large error limit does not permit a critical comparison of this value to data obtained by other techniques. An uncertainty of this magnitude was most likely due to the stated<sup>7</sup> weak intensities. To allow a comparison of the microwave value of the energy difference to results from other methods, a more accurate study of transition intensities in cyclohexyl fluoride has been done and the conclusions

are reported here. Particularly interesting is the fact that there is little if any difference in the conformational free-energy difference in the gas phase and in solution.

In the previous study,<sup>7</sup> the ratios of unsaturated peak intensity coefficients  $\gamma_0$  were determined using the experimental procedure described by Esbitt and Wilson.<sup>8</sup> To extract the conformational energy difference from these data, it was necessary to assume that the line widths of the compared transitions were equal. In the present study, the approach used was that of Harrington<sup>9,10</sup> who introduced an intensity coefficient  $\Gamma$  and considered its properties, particularly its dependence on microwave power density. He found that under certain conditions of power saturation, the signal at a peak absorption frequency is directly proportional to the population density of the lower level of the transition. These conditions also yield a significant increase in signal strength over that obtained in measurements of  $\gamma_0$ . The latter measurements must be made at low power levels to ensure that the power-dependent coefficient  $\gamma$  has reached its limiting value  $\gamma_0$ . For a

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(8) A. S. Esbitt and E. B. Wilson, Jr., *Rev. Sci. Instrum.*, **34**, 901 (1963).

(9) H. W. Harrington, *J. Chem. Phys.*, **46**, 3698 (1967).

(10) H. W. Harrington, *ibid.*, **49**, 3023 (1968).

given sample pressure, the signal obtained using the maximum signal conditions outlined by Harrington<sup>9,10</sup> is roughly six times larger than that produced for the same transition at powers low enough so that  $1.0 > \gamma/\gamma_0 > 0.99$ .

### Experimental Section

The intensity coefficient  $\Gamma$  can be written as the product  $\Gamma = \eta\phi$ .<sup>9,10</sup> The parameter  $\eta$  contains the energy level population as a factor. Thus, the ratio of  $\eta$  for two transitions, one from each conformer, is the quantity of interest here. The function  $\phi$  depends on the microwave power density in the absorption cell, the power saturation coefficient, and the attenuation constant or "insertion loss" of the cell. Qualitatively,  $\phi$  approaches the limiting value  $\Phi = 0$  at both high and low extremes of power and has a maximum value  $\Phi_{\max}$  at an intermediate power. The closed form expression<sup>10</sup> for  $\Phi$  is rather complicated. However, the value of  $\Phi_{\max}$  for any transition depends only on the cell insertion loss at the transition frequency and can be determined to much better than 1% from the empirically determined relationship

$$\log \Phi_{\max} = -0.22 - U/40 \quad (1)$$

where  $U$  is the insertion loss in decibels.

Intensity measurements were made with a Hewlett-Packard 8400C microwave spectrometer. This instrument incorporates a microwave bridge which permitted the microwave power in the absorption cell to be varied while the power level at the crystal detector was set to the same value for all measurements. With the bridge used in this way, the output signal was directly proportional to the intensity coefficient  $\Gamma$ .

$$S = G\Gamma L_e/P_{ei}^{1/2} \quad (2)$$

$G$  is an absolute "gain factor" which is a characteristic of the spectrometer and its operating conditions. The experiment was conducted such that the value of  $G$  was the same for each transition involved in a relative intensity measurement.<sup>11</sup>  $L_e$  is the effective absorption path length and is related to the physical length  $L$  by  $L_e = L(\lambda_e/\lambda)$  where  $\lambda_e$  and  $\lambda$  are, respectively, the radiation wavelength in the absorption cell and in free space.  $P_{ei}$  is the microwave power at the exit of the absorption cell with the power at the detector crystal set to the value used during the intensity measurements but with no power flowing in the balance arm of the bridge.

Since  $S$  is directly proportional to  $\Gamma$  and thus to  $\Phi$ , adjustment of the power in the absorption cell until a maximum signal was obtained ensured that  $\Phi = \Phi_{\max}$  for all measurements. For the intensity measurements, the spectrometer was operated in the fixed frequency mode at a peak absorption frequency. This allowed the use of longer detection system time constants, resulting in increased signal-to-noise ratios.

In terms of experimental parameters, the ratio of  $\eta$  for two transitions  $i$  and  $j$ , one from each of the two conformers, could be expressed as

$$\eta(i)/\eta(j) = [S_{\max}(i)/S_{\max}(j)][P_{ei}(i)/P_{ei}(j)]^{1/2} \times [\Phi_{\max}(j)/\Phi_{\max}(i)] \quad (3)$$

Insertion loss measurements to determine  $\Phi_{\max}$  through eq 1 and power measurements to determine  $P_{ei}$  were made using standard microwave techniques; these factors contributed only a few per cent correction to the measured signal ratio because of the low voltage standing wave ratio and weak frequency dependence of the insertion loss of the absorption cell used.

The sample of cyclohexyl fluoride was obtained from Columbia Organic Chemical Co. The sample as received was sufficiently pure for the microwave work. Sample pressure in the absorption cell was adjusted to about 30 mTorr for the intensity measurements. The absorption cell temperature was  $298 \pm 1^\circ\text{K}$ .

### Conformational Energy Difference

The expression for  $\eta$  can be written

$$\eta = (4\pi^3 h^2 ab/3ck^2)^{1/2} T^{-1} \mu_{ij} \nu_0^2 n_i (2\pi\Delta\nu t)^{-1/2} \quad (4)$$

(11) An assumption which is implicit here is that the value of  $G$  is independent of the microwave frequency as long as the rectified dc crystal current is kept at a constant value. This assumption has been tested in our laboratory at specific frequencies in the range 26.5–40.0 GHz and appears to be valid to within about 1%.

where  $\nu_0$  is the peak absorption frequency,  $T$  is the absolute temperature,  $\mu_{ij}$  is the dipole moment matrix element for the  $i \rightarrow j$  transition,  $n_i$  is the population density for the lower level of the transition,  $\Delta\nu$  is the unsaturated transition half-width at half-maximum intensity, and  $t$  is the population relaxation time. The values of  $\mu_{ij}$  were calculated using the asymmetric rotor constants and dipole moment values reported by Pierce and coworkers.<sup>6,7</sup> It was assumed that the value of  $2\pi\Delta\nu t$  was the same for both transitions in a given pair.<sup>12</sup> The population density ratios and the experimental ratios from which these were calculated are listed in Table I.

**Table I.** Experimental Energy Level Population Density and  $\eta$  Ratios

Transitions <sup>a</sup>	Frequencies, MHz	$\eta_a/\eta_e$	$n_a/n_e$
3 <sub>12</sub> -4 <sub>22</sub> (a)	22791.76	0.302	0.668
5 <sub>33</sub> -6 <sub>34</sub> (e)	22997.02		
3 <sub>21</sub> -4 <sub>31</sub> (a)	24551.82	0.310	0.654
5 <sub>32</sub> -6 <sub>33</sub> (e)	23597.36		
3 <sub>13</sub> -4 <sub>23</sub> (a)	24093.40	0.200	0.631
5 <sub>23</sub> -6 <sub>24</sub> (e)	24371.32		

<sup>a</sup> Axial conformer (a); equatorial conformer (e).

The population density of an energy state  $i$  is given by

$$n_i = Ng_i \exp(-W_i/kT)/Q \quad (5)$$

$N$  is the total molecular density. The statistical weight factor  $g_i$  can be taken as  $2J_i + 1$  where  $J_i$  is the principal rotational quantum number,  $Q$  is the molecular partition function, and  $W_i$  is the energy difference between the state  $i$  and the ground state. Since measurements were made on vibrational ground state transitions, only the rotational energy  $W_{iR}$  and, for levels of the higher energy conformer, the conformational energy  $W_c$  contribute to  $W_i$ . It is clear that  $W_c$  is the difference in energy of the vibrational ground states of the two conformers in their lowest rotational state.

Table II contains the value of  $W_c$  calculated from the

**Table II.** Experimental Values for the Axial-Equatorial Energy Difference  $W_c$  in Cyclohexyl Fluoride

Transitions <sup>a</sup>	$W_c$ , <sup>b</sup> cal/mol
3 <sub>12</sub> -4 <sub>12</sub> (a)	243 ± 8
5 <sub>33</sub> -6 <sub>34</sub> (e)	
3 <sub>21</sub> -4 <sub>31</sub> (a)	255 ± 14
5 <sub>32</sub> -6 <sub>33</sub> (e)	
3 <sub>13</sub> -4 <sub>23</sub> (a)	279 ± 15
5 <sub>23</sub> -6 <sub>24</sub> (e)	
$\Delta\nu = 259 \pm 28$ cal/mol	

<sup>a</sup> Axial conformer (a); equatorial conformer (e). <sup>b</sup> Uncertainties listed for the individual values reflect only the precision of the measured intensity ratios. The uncertainty in the average value includes effects of systematic errors also (see text).

data for the three pairs of transitions studied. The precision of the measured intensity ratios was good and the error estimated from their reproducibility was 1–2%. This corresponds to a 7–15 cal/mol contribution to the uncertainty in the individual values of  $W_c$ . Uncertainties which contribute to the 36-cal/

(12) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill, New York, N. Y., 1956, pp 350–352.

mol range in the three values of  $W_c$  result from uncertainties in experimental values of  $P_{ei}$  and  $U$  which are estimated as  $\pm 10$  and  $\pm 18$  cal/mol, respectively. Reported errors in the experimental dipole moment values contribute  $\pm 10$  cal/mol to the total uncertainty in  $W_c$ . The uncertainty of 28 cal/mol listed for the average value of  $W_c$  is the rms value of the uncertainties from the sources of error mentioned. The rms deviation of the three values of  $W_c$  from their average is 15 cal/mol.

### Discussion

The conformational energy difference  $W_c$  determined in this work is a property of the isolated molecule, free from the effect of intermolecular interactions. Comparison of this result to nmr data, obtained from studies of solutions, should then provide some measure of the effect of liquid-phase intermolecular interactions on the conformational preference. The nmr work determined values for the conformational free-energy difference  $\Delta F = F_{ax} - F_{eq}$ . The comparable quantity in the gas phase is related to  $W_c$  by

$$\Delta F = W_c + RT \ln (Q_{eq}/Q_{ax}) \quad (6)$$

where  $Q_{eq}$  and  $Q_{ax}$  are the internal partition functions of the individual equatorial and axial conformers, respectively.<sup>13</sup> The second term in eq 6 can be represented as the sum of two terms, one due to rotation  $\Delta F^{rot}$  and one due to vibration  $\Delta F^{vib}$ . The rotational constants given in ref 6 and 7 can be used to calculate  $\Delta F^{rot} = 0.210T$  cal/mol.<sup>14</sup> Calculation of  $\Delta F^{vib}$  would require knowledge of the differences in the fundamental vibrational frequencies of the two conformers, particularly those at low frequency.<sup>14</sup>

Measurements of chemical shifts<sup>2-4</sup> and measurements of the ratios of areas under resolved axial and equatorial resonances<sup>3,5</sup> have both been used to estimate  $\Delta F$ . The latter method should give the most unambiguous result and area ratio data will be compared to the microwave value. A comment on results from the two nmr methods will be given below. Proton resonance area measurements gave a  $\Delta F$  value of  $276 \pm 15$  cal/mol at 100 MHz and 187°K,<sup>5</sup> identical with a value determined earlier<sup>3</sup> at 60 MHz and 185°K. The solvent was CS<sub>2</sub> in both studies. Fluorine spectra yielded an area ratio of  $1.75 \pm 0.05$  in the temperature range 212–227°K and  $1.96 \pm 0.05$  at 185°K.<sup>3</sup> Values of  $\Delta F$  calculated from the latter data are  $252 \pm 12$  cal/mol at 212°K and  $248 \pm 12$  cal/mol at 185°K. The solvent

(13) Of course,  $Q = Q_{eq} + \exp(-W_c/RT)Q_{ax}$ . See T. L. Hill, "Statistical Thermodynamics," Addison-Wesley, Reading, Mass., 1962, p 182.

(14) G. Herzberg, "Infrared and Raman Spectra," Van Nostrand, Princeton, N. J., 1945, Chapter V.

was CClF<sub>3</sub>. The difference in solvents may account for part of the difference in  $\Delta F$  from the proton and fluorine resonance measurements. At 185°K, the average of the proton and fluorine resonance values is  $262 \pm 20$  cal/mol. If  $\Delta F^{vib}$  is neglected, then  $\Delta F = 298 \pm 28$  cal/mol in the gas phase at 185°K. Thus, the difference between the gas-phase value (excluding  $\Delta F^{vib}$ ) and the solution value for  $\Delta F$  is within the combined error limit of  $\approx 40$  cal/mol.

A value of 170 cal/mol for  $\Delta F$  in the gas phase was derived from electron diffraction data.<sup>1</sup> The usefulness of this result is limited since the temperature was not specified and the effect of structural assumptions, required for the analysis, could not be estimated. It can be used, however, to provide at least a rough estimate for  $\Delta F^{vib}$  and improve the comparison between the gas-phase and solution values given in the last paragraph. An observation temperature of 300°K was assumed (much lower temperature would be unlikely because of vapor pressure limitations) and an approximate estimate of the temperature dependence of  $\Delta F^{vib}$  was made to arrive at the estimate  $\Delta F^{vib} \approx 50$  cal/mol at 187°K. Thus, the difference between the gas-phase and solution values is reduced when vibrational effects are taken into account in this way. The magnitude of this estimate of  $\Delta F^{vib}$  is probably somewhat too large, however, since it implies differences between the vibrational frequencies of the two conformers which appear to be unusually large.

At temperatures near 300°K, nmr chemical shift methods give  $\Delta F$  values near 150 cal/mol.<sup>3,4</sup> Bovey and coworkers<sup>3</sup> combined chemical shift results with those from area ratio measurements to determine a value of  $1.05 \pm 0.10$  eu for the conformational entropy difference  $\Delta S = S_{ax} - S_{eq}$ . In order for chemical shift methods to yield good estimates for a  $\Delta F$ , it is necessary that the chemical shifts of the individual axial and equatorial resonances be independent of temperature. This assumption has been questioned, however.<sup>5,15</sup> The reported<sup>3</sup> temperature dependence of fluorine area ratios can be used to calculate an independent estimate of  $-0.1 \pm 0.5$  eu for  $\Delta S$  in cyclohexyl fluoride. The uncertainty is larger than that associated with the use of chemical shift data, in part because of the small temperature range over which ratio measurements were made. However, no assumptions are required in deriving the entropy difference. Also, the entropy difference derived in this way is more in line with those indicated for other cyclohexyl halides according to results reported by Jensen and Beck.<sup>15</sup>

(15) F. R. Jensen and B. H. Beck, *J. Amer. Chem. Soc.*, **90**, 3251 (1968).