

Lawrence Berkeley National Laboratory

Recent Work

Title

POTENTIAL ENERGY AS A FUNCTION OF INTERNAL ROTATION IN CFC1 Br-CFC1 Br NMR MEASUREMENTS

Permalink

<https://escholarship.org/uc/item/2zt2d7k7>

Authors

Thompson, Douglas S.
Newmark, Richard A.
Sederholm, Charles H.

Publication Date

1962-02-01

UNIVERSITY OF
CALIFORNIA

Ernest O. Lawrence

*Radiation
Laboratory*

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545*

BERKELEY, CALIFORNIA

UCRL-10093

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

POTENTIAL ENERGY AS A FUNCTION OF INTERNAL ROTATION
IN CFCl Br-CFCl Br BY NMR MEASUREMENTS

Douglas S. Thompson, Richard A. Newmark, and Charles H. Sederholm

February 1962

Potential Energy as a Function of Internal Rotation
in CFClBr-CFClBr by NMR Measurements

Douglas S. Thompson, Richard A. Newmark, and Charles H. Sederholm
Department of Chemistry and Lawrence Radiation Laboratory
University of California, Berkeley 4, California

ABSTRACT

The NMR spectrum of CFClBr-CFClBr is reported as a function of temperature from 177°K to 300°K. The high temperature spectrum is analyzed in terms of a superposition of the spectra of the meso and dl isomers, each in rapid rotation about the C-C bond; the low temperature spectrum on the basis of a superposition of the spectra of the three rotamers of each of the two isomers. The gauche coupling constant between fluorine atoms in this compound is 21.5 ± 0.5 cps. Chemical shifts for the fluorine atoms were different for the three rotamers. Fluorine atoms gauche to one fluorine and one chlorine atom are at the highest field, and fluorine atoms gauche to one fluorine and one bromine atom are at the lowest field.

By observing the relative areas of peaks at low temperature, relative energies of the three potential minima for each isomer are calculated. High temperature areas determined the relative amounts of the two isomers. Using, in addition, chemical shift data from the low temperature spectra, spectra of this mixture of isomers have been calculated as a function of temperature assigning various potential barriers to internal rotation. By comparing the calculated spectra

with those observed at various temperatures, several of the potential barriers to internal rotation have been assigned. In each isomer, the three potential minima vary by at most 450 cal/mole. The potential maxima which can be measured are all approximately 10.0 ± 0.5 kcal/mole above the potential minima.

A great deal of work has been done in microwave spectroscopy to measure the barriers to internal rotation in a series of molecules in an attempt to understand the causes of these barriers.¹ Due to inherent restrictions in the microwave method only barriers of methyl groups rotating against various other groups have been measured by this technique. In all substituted ethanes containing a methyl group, the measured barriers have turned out surprisingly constant at approximately 3 kcal/mole. This has led people to postulate that the main contribution to these barriers arises from such things as bond multipoles interacting with bond multipoles, or non-cylindrical electron distributions around the C-C bond. Moreover, most people are in agreement that little if any of these barriers arises from strictly steric repulsions. It has been felt that as larger atoms are added to both ends of the ethane molecule, a sizable contribution from steric repulsion might result. Barriers are known for two substituted ethanes where halogens have been substituted on both ends, and in these two cases, the barriers

are substantially above the 3 kcal/mole value; $\text{CF}_3\text{CH}_2\text{F}$ at 4.2 kcal/mole, and CCl_3CCl_3 at 10.8 kcal/mole.¹ The further investigation of such compounds may hopefully put the steric contribution to the barrier on a quantitative basis.

If the barrier to internal rotation is approximately 10 kcal/mole, and fluorine or hydrogen atoms are included in the molecule, nuclear magnetic resonance techniques provide a useful tool for measuring the potential barrier. With a barrier of this approximate value, it is relatively simple to freeze out the various rotamers so that the NMR spectrum corresponds to a superposition of the spectra of the three rotamers. Investigation of the NMR spectrum as a function of temperature can then give several pieces of information. Coupling constants between magnetic nuclei on the two ends of the molecule can be measured for trans and gauche orientations. The chemical shift of a given magnetic nucleus can be measured as a function of the relative angular orientation of the opposite end of the molecule. By measuring the relative areas of the lines due to the three rotamers, the relative energies of the three potential minima can be determined. Finally, by comparing the observed spectra at transition temperatures with calculated spectra assuming various barriers to internal rotation, a good deal of information can be gained concerning the height of the various potential maxima.

Sample

The sample was provided by Dr. Paul Resnick of this department. The microboiling point of the compound was 138°C in good agreement with the value tabulated by Lovelace, Rausch, and Postelnek² of 139.7°C. A freezing-point-depression-of-benzene determination of the molecular weight gave a value of 339 g/mole. This value is considered to be within the experimental accuracy of the theoretical value. All of the peaks in the NMR spectra can readily be assigned to the two isomers with no observable resonances corresponding to impurities. The sample was diluted with carbon disulfide to a final concentration of approximately 5% by volume, and sealed in a 5 mm, thin walled NMR tube.

Experimental

The spectra were taken on a Varian HR-60 spectrometer operating at 56.4 mcs. This instrument was equipped with a base line stabilizer and integrator, thereby eliminating any difficulties due to probe imbalance as the temperature of the insert was changed.

The insert was constructed in this laboratory. It was dewared and had provisions for passing cooled nitrogen down an outer compartment, then up around the sample. The bottom of the assembly was thermally insulated from the metallic probe by a quartz plug. Quartz was used here so that the positioning of the receiver coil was not drastically changed as the temperature was lowered. A dewared nitrogen inlet

line was used to carry the coolant from a liquid nitrogen boiler to the insert. The cooling gas outlet was attached to a high volume vacuum system to increase the flow rate through the insert without using prohibitive pressures on the high pressure side. Provisions for spinning the sample were incorporated into the insert design.

A copper-constantan thermocouple was placed in the insert at a point in the nitrogen path just ahead of the sample. The temperature of this thermocouple was compared with the temperature of a thermocouple placed in a dummy sample tube which was inserted in the probe. It was found that if the temperature was held a few degrees below the desired value for a few minutes and then brought to the desired value, the temperature of the permanent thermocouple and that of the sample thermocouple were identical to within an accuracy of $\pm 2^\circ\text{K}$. All spectra and integrals reported here are reproducible to within the limits imposed by the signal-to-noise ratio.

Results

The experimental spectra as a function of temperature are shown in Fig. 1-4. The room temperature spectrum consists of two sharp peaks. The separation of the two peaks is 43.4 ± 0.2 cps. At room temperature and above, the high field peak contains 52.8% of the total integrated area. The chemical shifts from an arbitrary zero and the relative intensities of the low temperature peaks shown in Fig. 1 are tabulated in Table I. The integrated areas were obtained by using a planimeter on a large number of good spectra and taking the average.

The root-mean-square deviation from the mean was approximately 1% and the most probable error 0.2%. However, systematic errors due to overlap of the lines probably make some of these integrated areas more uncertain than the above figures indicate.

Assignment

The compound under investigation has two asymmetric carbon atoms. There is therefore the possibility of two different isomers, a meso form and a dl form. At low temperatures, both of these isomers will consist of three rotamers. These rotamers are depicted in Figure 5.

At high temperatures, when free rotation about the carbon-carbon bond is possible, the two fluorine atoms in each isomer will appear to be chemically equivalent due to time averaging of the nuclear environment; however, a fluorine atom in one isomer will be chemically different from a fluorine atom in the other. The predicted high temperature spectrum of a mixture of these two isomers should then consist of two lines, one from each isomer. Since the preparation of this compound was such that a mixture of the isomers should result, the room temperature spectrum is readily understood as being the high temperature spectrum of a mixture of the two isomers. From the integrated areas the relative proportion of the two isomers is 47.2% to 52.8%. Without further analysis, it is not apparent which peak corresponds to which isomer.

At sufficiently low temperatures, the spectrum should be the superposition of the spectra of the three different rotamers of each of the two isomers. If some of these rotamers are at a

much higher energy than others, their population may be so small that the lines due to said rotamers will be unobservable. Theoretically, we would predict that rotamer Ia should give a single line, since by symmetry the equilibrium dihedral angle between the fluorine atoms must be exactly 180° , hence making the two fluorine atoms chemically equivalent. Rotamers Ib and Ic are mirror images of each other and hence should yield identical spectra. In these two rotamers, the two fluorine atoms are not identical and hence should lead to two resonances. By analogy with other compounds,³ one might expect the spins of these two fluorine atoms to be coupled resulting in a pair of doublets with equal splitting. Rotamer IIA has two chemically equivalent fluorine atoms irrespective of the dihedral angle between the fluorine atoms. The same is true for rotamers IIB and IIC. These three rotamers should then yield three singlets in the spectrum. Hence, the combined spectrum of the three rotamers of the two isomers should be four singlets and a pair of doublets. This is precisely the spectrum observed at 177°K as shown in Fig. 1. The two doublets should have equal areas since they are due to equal numbers of fluorine atoms in rotamers Ib and Ic. The nonequivalence of these two areas is due to errors in area measurements brought about by overlap of the various lines and base line ambiguities. The splitting of the two doublets should be identical which it is, within the limits of experimental error. The coupling constant between the gauche fluorine atoms in rotamers Ib and Ic is 21.5 ± 0.5 cps.

Referring to the lettering scheme in Fig. 1, peaks B, C, F and G must arise from rotamers Ib and Ic because of the doublet nature. The sum of the areas of these four peaks is 19.3% of the total area. Since from the high temperature spectrum, we know that isomer I must make up either 52.8% or 47.2% of the total area, this means rotamer Ia must account for either 33.5% or 27.9% of the total. Hence, rotamer Ia must be responsible for either peak D or E. The other of these two peaks must be associated with some rotamer of isomer II, and since the total area of these two peaks is 50.4%, the area of the peak associated with some one rotamer of isomer II must be either 16.9% or 22.5% of the total area. Since the peak associated with rotamer Ia must have a greater area than the peak associated with said rotamer of isomer II, and since D is greater in area than E, peak D must be associated with rotamer Ia.

We are now in a position to more accurately assign the room temperature spectrum. Isomer I is responsible for peaks B, C, D, F and G. The high temperature spectrum of this isomer, which consists of a single peak whose chemical shift is the time weighted average of the chemical shifts of the above listed peaks should be someplace near peak D. Isomer II is responsible for peaks A, E, and H. Since the rotamer responsible for peak H is less populated than the other two rotamers even at room temperature, the high temperature time weighted average peak due to isomer II should lie somewhat downfield from peak E, and in fact, downfield from peak D. Hence, we can tentatively assign the low field, room temperature peak to isomer II and the high

field one to isomer I. The correctness of this assignment is checked at a later point in the argument. With this tentative assignment, we conclude that isomer II makes up 47.2% of the mixture, and isomer I, 52.8%. This then implies that peak D has an area of 33.5% and peak E an area of 16.9%. The assignment of the low temperature spectrum is summarized in Table II.

Using the Boltzman energy distribution, one can calculate free energies associated with the various rotamers, using as an energy zero the energy of the lowest energy rotamer of each isomer. These are also tabulated in Table II.

It is now possible to check both the tentative room temperature assignment and the low temperature areas and chemical shifts by calculating the expected room temperature separation from the low temperature data. The position of the room temperature peak of a given isomer is given by⁵:

$$v = \frac{\sum_{n=1}^3 v_n e^{-E_n/RT}}{\sum_{n=1}^3 e^{-E_n/RT}} \quad (1)$$

where v is the room temperature resonant frequency of an isomer, v_n is the resonant frequency of rotamer n of that isomer, and E_n is the free energy associated with rotamer n of that isomer.

Using the data tabulated in Table II, we find that at $T = 298^\circ\text{K}$ $v_I = 198.0$ cps, $v_{II} = 152.0$ cps, yielding a predicted separation of 46.0 cps. This is to be compared with the experimental separation of 48.4 ± 0.2 cps. Since this is a fairly

sensitive function of the low temperature areas and chemical shifts, the observed agreement is excellent.

It is to be noted that in this calculation, isomer I gives rise to the high field peak as was qualitatively predicted earlier. If alternatively, the high field peak at room temperature had been assigned to isomer II, the present calculation would have yielded $\nu_I = 197.6$ cps, $\nu_{II} = 156.0$ cps, separation = 41.6 cps. In this case, ν_I comes out the high field peak in contradiction to the initial assumption. Hence, the tentative assignment of isomer I to the high field, room temperature peak is confirmed.

Referring to Fig. 5, peak D must correspond to rotamer Ia and peaks B, C, F, and G to rotamers Ib and Ic. In rotamer Ia, the fluorines are gauche to Br and Cl atoms. This is also true of the fluorine atoms in rotamer IIa. Hence, the chemical environment of the fluorine atoms in rotamers Ia and IIa are very similar, and on this basis, it seems reasonable to assign peak E to rotamer IIa.

Of rotamers IIb and IIc, one is 400 cal/mole lower in energy than the other. According to Mizushima⁴ the energy difference between the various rotamers seems to be determined by steric considerations and/or bond-dipole bond-dipole interactions. In totally halogen substituted ethanes, both of these phenomena lead to the same conclusions concerning the relative stabilities of the three rotamers. On this basis, it appears that IIb should be lower in energy than IIc since IIb should have less steric interaction energy and less dipole-dipole interaction energy. Hence, we assign peak A to IIb and peak H to IIc.

In isomer II, a fluorine atom gauche to F and Br is to low field and a fluorine atom gauche to F and Cl is to high field of one gauche to Br and Cl. It is therefore reasonable to assume that the F atoms in rotamers Ib and Ic gauche to F and Br are responsible for peaks B and C and the fluorine atoms gauche to F and Cl are responsible for peaks F and G.

Barriers to Internal Rotation

At a temperature sufficiently high so that the molecules change from one rotational configuration to another in a time short with respect to the length of time necessary for an NMR transition, the fluorine spectrum consists of peaks corresponding to average environments of the fluorine atoms. When the time characteristic of rotation is decreased by lowering the temperature, to a time long compared to the NMR transition time, the fluorine spectrum consists of peaks corresponding to the fluorine atoms in the individual rotamers. At intermediate temperatures, the spectrum will be intermediate between these cases. This intermediate spectrum can be calculated from the Bloch equations, given the chemical shifts of the fluorine atoms in each of the rotamers, the relative populations of molecules existing as each rotamer, and the transition probabilities between the various rotamers. The chemical shifts of the fluorine atoms in the various rotamers are known. If one assumes that the free energies corresponding to the various rotamers do not change much with temperature, one can readily calculate the relative population of molecules in each of the rotamers at any given temperature. The transition probabilities between the

various rotamers can be calculated from absolute reaction rate theory. The rate constant for such a unimolecular reaction is:

$$K = \kappa \frac{kT}{h} \frac{f^\ddagger}{f} e^{-\Delta E^\ddagger/RT} \quad (2)$$

where κ is the transmission coefficient, f^\ddagger is the partition function of the activated complex (in this case, the eclipsed form of the molecule), f is the partition function for the individual rotamer which is reacting, and ΔE^\ddagger is the activation energy, i.e., the energy of the eclipsed form minus the energy of the staggered form. The partition functions for the eclipsed and staggered forms of the molecule under consideration are very nearly equal and will therefore cancel out. Hence:

$$K = \kappa \frac{kT}{h} e^{-\Delta E^\ddagger/RT} \quad (3)$$

We could make various assumptions for κ . The two limiting cases are as follows: (1) $\kappa = 1$ which corresponds to a picture where every time a molecule is excited to an eclipsed form, it continues to rotate in the same direction and finally ends up in the next staggered form. This would seem to be a poor approximation since the length of time necessary for rotational deactivation in the liquid phase is probably much longer than the rotational frequency. (2) κ is assigned a value which corresponds to the following physical situation. Each time a molecule obtains sufficient energy to mount a barrier, it retains this energy for several vibrations or rotations, as the case may be, and finally has equal probability of falling into

every potential minima to which it has access. When all three maxima are the same height, this corresponds to $\kappa = 1/3$. In other cases, κ is not a constant, but is easily written down for a given set of barriers. Although this is probably not the exact case, it should be a much better approximation. The actual case lies someplace between ^{these} two approximations. The choice of approximation is not terribly critical. If case 1 were chosen rather than case 2, all of the calculated barriers would be approximately 0.5 kcal higher.

The Bloch equations as applied to this phenomenon are⁵:

$$\alpha_j = T_{2j}^{-1} - i(\omega_j - \omega) \quad (4)$$

$$\frac{dG_j}{dt} + \alpha_j G_j = -i\gamma H_1 M_{0j} + \sum_k (\tau_{kj}^{-1} G_k - \tau_{jk}^{-1} G_j) \quad (5)$$

$$G = \sum_j G_j \quad (6)$$

where α_j is a dummy variable, T_{2j} is the transverse relaxation time for a fluorine in position j , ω is the radio frequency being used for excitation of the NMR transition, ω_j is the resonant frequency of a fluorine in position j , G_j is the complex component of the magnetization due to the fluorine atoms in the j^{th} position, G is the total complex magnetization of the sample, the imaginary part of G corresponds to the absorption signal, γ is the magnetogyric ratio for fluorine atoms, H_1 is the magnitude of the rf field, and M_{0j} is the maximum magnetic moment of the fluorine atoms in the j^{th} position. τ_{kj}^{-1} is equal to the transition probability for a fluorine atom changing from position k to position j . From absolute reaction

rate theory, we set:

$$\tau_{kj}^{-1} = \kappa \frac{kT}{h} e^{-(E_{kj} - E_k)/RT} \quad (7)$$

In our particular application, at both high and low temperatures, the lines are very narrow compared to the widths of the lines in the transition region. We can therefore set $\tau_{2j}^{-1} = 0$ for all j with little error in the calculated spectra.

Consider a potential energy curve as shown in Fig. 6. The following reasoning can be called upon to evaluate τ_{12}^{-1} . In order for a molecule in configuration 1 to change to configuration 2, it must gain an energy at least as great as E_6 . The fraction of molecules in configuration 1 with energy greater than E_6 is $\exp[-(E_6 - E_1)/RT]$ and each of these molecules will have a one third probability of falling into configuration 2. Hence:

$$\tau_{12}^{-1} = \frac{1}{3} \frac{kT}{h} e^{-(E_6 - E_1)/RT}$$

On the other hand, the fraction of molecules in configuration 1 with energy between E_4 and E_6 is $\exp[-(E_4 - E_1)/RT] - \exp[-(E_6 - E_1)/RT]$, and each of these molecules has a probability of one half of falling into configuration 3. The fraction of molecules in configuration 1 with energy greater than E_6 is $\exp[-(E_6 - E_1)/RT]$ and each of these molecules has a probability of one third of falling into configuration 3. Hence:

$$\tau_{13}^{-1} = \frac{1}{2} \left[e^{-(E_4-E_1)/RT} - e^{-(E_6-E_1)/RT} \right] + \frac{1}{3} \left[e^{-(E_6-E_1)/RT} \right]$$

By similar considerations:

$$\tau_{23}^{-1} = \frac{1}{3} e^{-(E_6-E_2)/RT}$$

$$\tau_{21}^{-1} = \tau_{23}^{-1}$$

$$\tau_{31}^{-1} = \frac{1}{2} \left[e^{-(E_4-E_3)/RT} - e^{-(E_6-E_3)/RT} \right] + \frac{1}{3} \left[e^{-(E_6-E_3)/RT} \right]$$

$$\tau_{32}^{-1} = \frac{1}{3} \left[e^{-(E_6-E_3)/RT} \right]$$

Putting in the observed values of ω_1 , ω_2 , ω_3 , E_1 , E_2 , and E_3 , one can now calculate the imaginary part of G as a function

of ω at various values of T , adjusting the values of E_4 , E_5 , and E_6 until a best fit of the experimental data is obtained. Actually, only two of the three unknown energies determine the spectrum of a single isomer using the above choice for κ . The spectrum is completely independent of the highest of the potential barriers. This can readily be seen since any staggered configuration can change into any other staggered configuration without traversing the highest of the potential barriers.

Such a calculation was carried out on an IBM 704, for each isomer, at several temperatures in the transition range, and for a variety of different values of E_4 , E_5 , and E_6 for each isomer. The calculated spectra for the two isomers were superimposed, and the resultant compared with the experimental spectra. The results of these comparisons are shown in Figs. 2, 3, and 4.

In isomer I, two maxima in the potential energy are identical by symmetry. If the third maximum is higher, the calculated spectrum would not be a function of its height by the argument above. If on the other hand, the maximum between configurations Ib and Ic is lower than the other two maxima, this would imply that peaks B, C, F, and G should collapse into a single peak at a lower temperature than peak D merges in with the other four. Unfortunately, a single peak resulting from the collapse of B, C, F, and G would lie almost on top of peak D and hence it is impossible to tell whether these five lines have all collapsed into one or whether B, C, F, and G have collapsed into one line which lies on top of peak D. It is

therefore only possible to determine the height of the smallest barrier to internal rotation in isomer I, and the spectrum is essentially not a function of the height of the other barrier(s). Hence, in our calculation for isomer I, all three barriers have been set equal.

As a first approximation, the three barriers for isomer II were equated. With this two parameter system, a fair fit of the experimental data was possible. However, when this approximation was made, peak H always came out insufficiently intense in the calculated spectra. It was thought that the low temperature integrations might be in error and that the energy associated with peak H might be considerably less than 450 cal/mole. A value of approximately 200 cal/mole was necessary to fit the intensity of peak H in the transition temperature region. However, a value of 200 cal/mole for the energy of the rotamer associated with peak H leads to a calculated separation of 25.0 cps between the room temperature peaks, to be compared with the experimental value of 48.4 ± 0.2 cps. This lack of agreement implies that the height of peak H at the transition temperatures cannot be accounted for by changing the value of the energy associated with that isomer.

The other method of making the calculated height of peak H larger is to increase the barriers on both sides of the rotamer corresponding to peak H, above the value of the third barrier. Again, with the assumed value for κ , changing the height of the highest of the three barriers does not change the calculated spectrum; hence, the barriers on either side of the rotamer associated with peak H were set equal in the calculation.

Of the five independent barriers, there are only three parameters which, when adjusted, will alter the calculated spectra. These are:

1. The height of the lowest barrier in isomer I.
2. The height of the barrier between the configurations corresponding to peaks A and E.
3. The height of the lower of the two barriers which are on either side of the rotamer corresponding to peak H.

By varying these three parameters, the calculated spectra were fitted to the observed spectra at 194°K, 207°K and 233°K to an accuracy of ± 0.5 kcal/mole. In Figs. 3, 4, and 5 are shown the observed spectra, the calculated spectra which best fit the observed spectra at each temperature, and the calculated spectra with each parameter varied by ± 0.5 kcal/mole from the best fit value. The values of the parameters which give the best fit at the three temperatures are listed in Table III.

The variation of the three parameters with temperature is probably due to (1) variation of the free energies associated with the various rotamers as a function of temperature, (2) inaccuracies in the approximation to κ , (3) inaccuracies in the temperature measurements. There may also be some error due to the long instrument response times necessitated by the signal-to-noise ratio. This would tend to decrease the apparent signal height of tall narrow peaks much more than of short broad ones.

Conclusions

Again referring to Fig. 6, and denoting the eclipsed configuration intermediate between rotamers Ia and Ib as Iab, a summary of the observed energy data is given in Table IV.

The coupling constant between the two fluorine atoms in this compound, when they are gauche to each other is 21.5 ± 0.5 cps. This is in general agreement with fluorine-fluorine coupling constants in other substituted ethanes where the substituted groups are large.³

The chemical shift of the fluorine atoms is partially determined by the rotational configuration of the molecule. A fluorine atom gauche to a F and a Cl atom is to higher field than one gauche to a Br and a Cl atom. A fluorine gauche to an F and a Br atom is to lower field still. In terms of high field shifting power of the individual neighboring atoms, this implies $Cl > F > Br$, an order which is somewhat surprising and difficult to explain.

The small differences between the energies of the three rotamers is intuitively somewhat surprising; however, this order of magnitude is quite common in halogen substituted ethanes in the liquid phase.⁴

Since the bromine atoms are the largest substituents in this compound, and hence should be responsible for the majority of the steric repulsion, it seems quite reasonable that rotamers Ib and Ic should be higher in energy than Ia since both Ib and Ic involve gauche bromine-bromine atom interactions whereas the

bromine atoms in Ia are trans to each other. In isomer II, it also seems reasonable that the rotamer with the lowest energy is IIb where the bromine atoms are trans to each other as is observed experimentally. An argument based on bond-dipole bond-dipole interactions yields similar conclusions for both isomers.

The magnitude of the barriers to internal rotation seem quite reasonable when compared with the barrier in CCl_3CCl_3 which is 10.8 kcal/mole.¹ From the data available, it is possible to draw a somewhat quantitative, empirical correlation between barriers to internal rotation and the substituted groups.

The near equivalence of all of the measurable barriers in the compound here investigated implies that to a first approximation, the barrier is only a function of the number and kind of substituted atoms, and not a sensitive function of their relative orientation. It seems reasonable therefore that the energy barrier might be expressible as a function of a single variable, this variable being an additive property of the substituted groups. This property of the substituted groups should be a measure of the steric energy for which that group is responsible. Such a property might be the difference between the distance of a substituted atom from the plane bisecting the C-C bond, and the covalent radius of that atom. Covalent radii were chosen rather than Van der Waal radii since the covalent radii are a measure of the atomic size whereas the Van der Waal radii are also a function of the attractive forces between atoms. Let us define a quantity $\Delta_1 = D_1 - R_1$ where D_1 is the distance

of the i^{th} atom from the plane bisecting the C-C bond and R_1 is the covalent radius of the i^{th} atom. In Table V are listed the values of this Δ for three halogens and hydrogen, assuming tetrahedral angles and normal covalent bond distances.

Figure 7 shows the barrier to internal rotation plotted against $\sum_{i=1}^6 \Delta_i$, the sum being taken over the six atoms attached to the C-C skeleton. This plot includes the data for all substituted ethanes for which barriers are known. Although the points on this curve fall in two bunches the plot seems to indicate some correlation between these two variables.

Acknowledgment. We wish to thank Dr. Paul Resnick of this department for the preparation of the compound used. We also wish to thank the A.E.C. for support of this research.

References

1. E. B. Wilson, Advances in Chemical Physics II, Interscience Publishers, Inc., New York 1959, and references cited therein.
2. A. M. Lovelace, Douglas A. Rausch, and William Postelnek, Aliphatic Fluorine Compounds, Reinhold Pub. Corp., New York, 1958.
3. L. Petrakis and C. H. Sederholm, J. Chem. Phys. 35, 1243 (1961).
4. S. Mizushima, Structure of Molecules and Internal Rotation, Academic Press, Inc., New York, 1954.
5. J. A. Pople, W. G. Schneider, and H. J. Bernstein, High Resolution Nuclear Magnetic Resonance, McGraw-Hill Book Company, New York, 1959, pp.218 ff.

Table I

Peak	Chemical shift in cps from lowest frequency peak	Integrated area (% of total area)
A	0.0	23.7
B	94.9	105.5 } 10.0
C	116.0	
D	205.3	50.4
E	214.2	
F	264.5	275.4 } 9.5
G	286.2	
H	368.1	6.6

Table II

Isomer	Peak	Chemical Shift (cps)	Area (%)	Free Energy (cal/mole)
I	D	205.3	33.5	0
	B-C	105.5	9.65	438
	F-G	275.4	9.65	438
II	A	0.0	23.7	0
	E	214.2	16.9	119
	H	368.1	6.6	450

Table III

Parameter	Barrier Energy (kcal/mole)			Best fit
	Temperature			
	194°K	207°K	233°K	
1	10.0	10.0	10.5	10.2
2	9.5	10.0	9.5	9.7
3	10.0	10.5	10.0	10.2

Table IV

Configuration	Energy (kcal/mole)	Configuration	Energy (kcal/mole)
Ia	0.000	IIa	0.119
Iab	$\geq 10.2^a$	IIab	9.7
Ib	0.438	IIb	0.000
Ibc	$\geq 10.2^a$	IIbc	$\geq 10.2^b$
Ic	0.438	IIc	0.450
Ica	$\geq 10.2^a$	IIca	$\geq 10.2^b$

^aThe energies of configurations Iab and Iac are equal. The energy of either Iab or Ibc is equal to 10.2 kcal/mole.

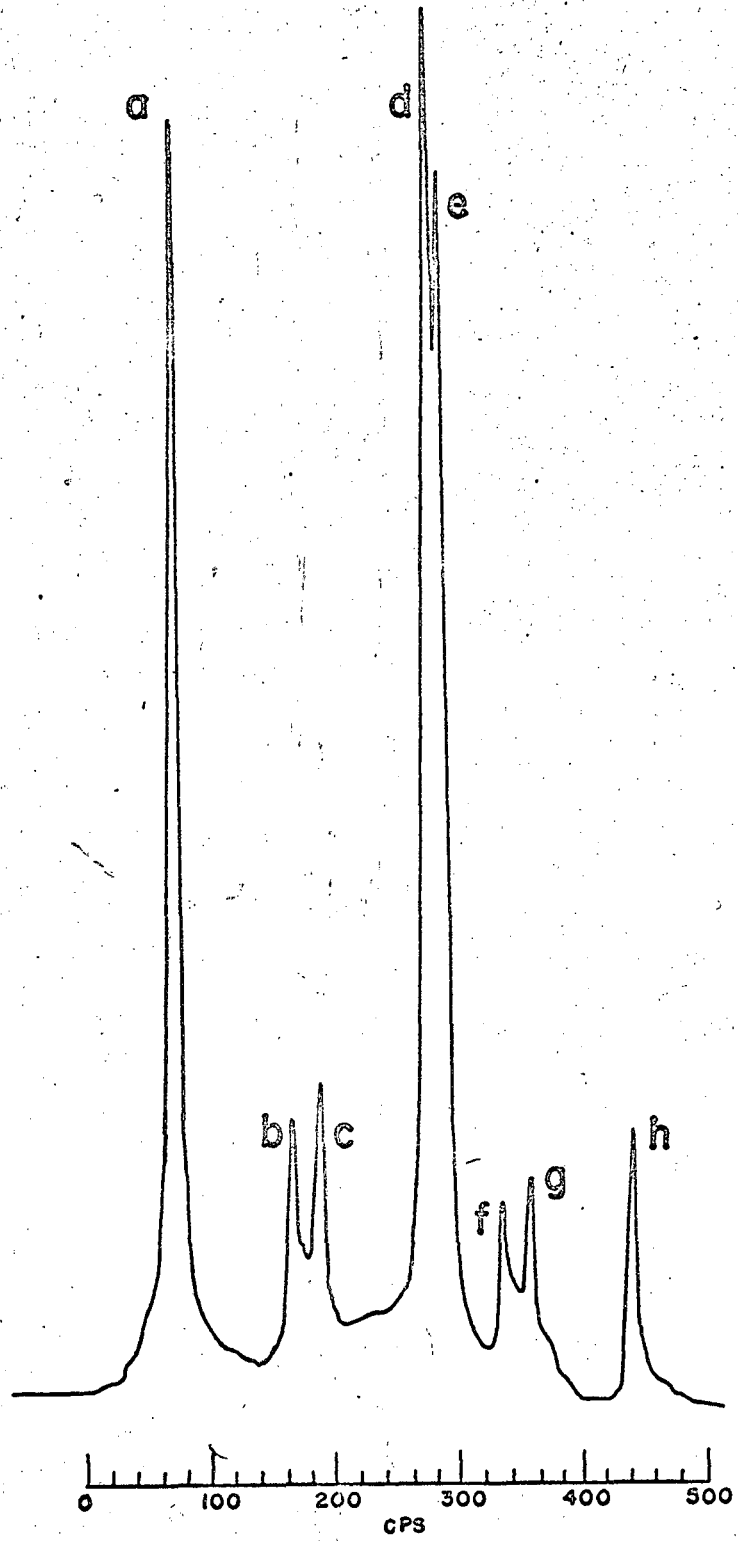
^bThe energy of IIbc or IIac is equal to 10.2 kcal/mole.

Table V

Substituent	$\Delta(\text{\AA})$
H	.82
F	.60
Cl	.37
Br	.24

Captions for Figures

- Fig. 1 Experimental NMR spectrum of CFClBr-CFClBr at 177°K .
- Fig. 2 Experimental and calculated NMR spectra of CFClBr-CFClBr at 194°K . The dotted lines in the experimental spectrum represent what the spectrum would be if the gauche coupling constant were zero; the approximation used in the calculation. The energies tabulated on each calculated spectrum correspond to parameters 1, 2, and 3 respectively of the text.
- Fig. 3 Experimental and calculated NMR spectra of CFClBr-CFClBr at 207°K . The energies tabulated on each calculated spectrum correspond to parameters 1, 2, and 3 respectively of the text.
- Fig. 4 Experimental and calculated NMR spectra of CFClBr-CFClBr at 233°K . The energies tabulated on each calculated spectrum correspond to parameters 1, 2, and 3 respectively of the text.
- Fig. 5 The three rotamers of the two isomers of CFClBr-CFClBr .
- Fig. 6 A possible potential energy curve as a function of dihedral angle.
- Fig. 7 Plot of barrier to internal rotation in substituted ethanes vs. sum of steric factors for substituents; see text.



MU - 24685

Fig. 1

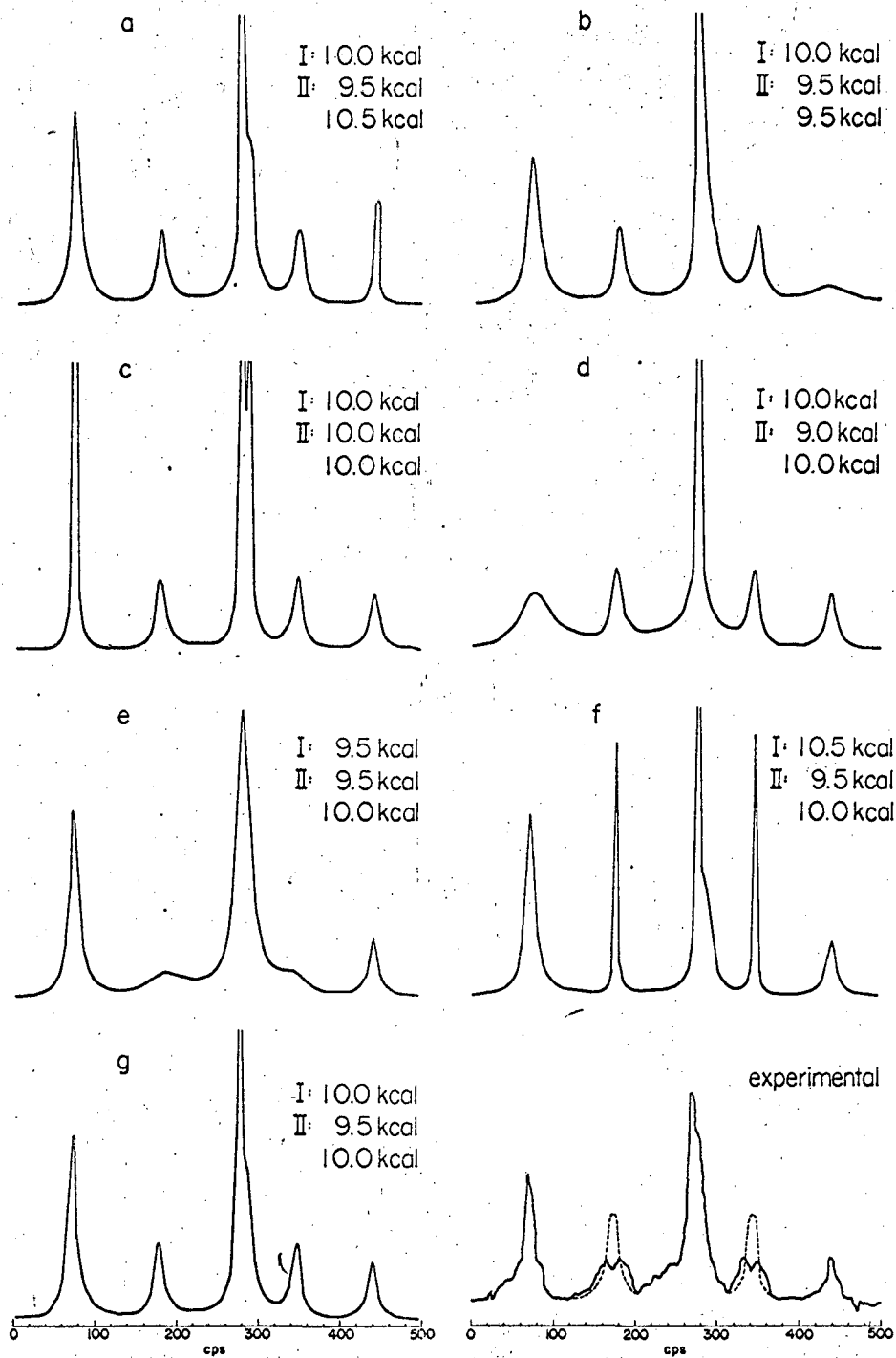


Fig. 2

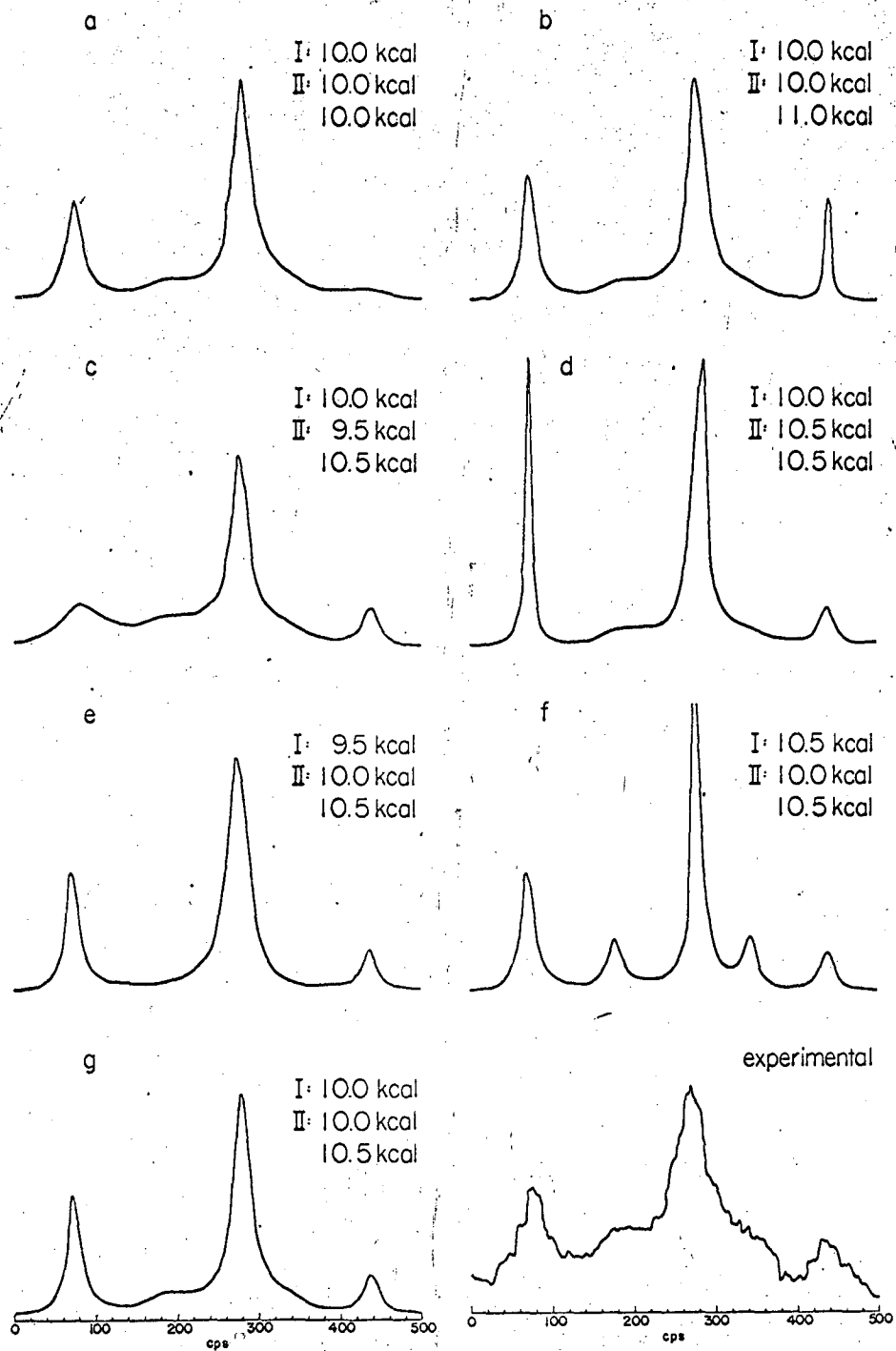


Fig. 3

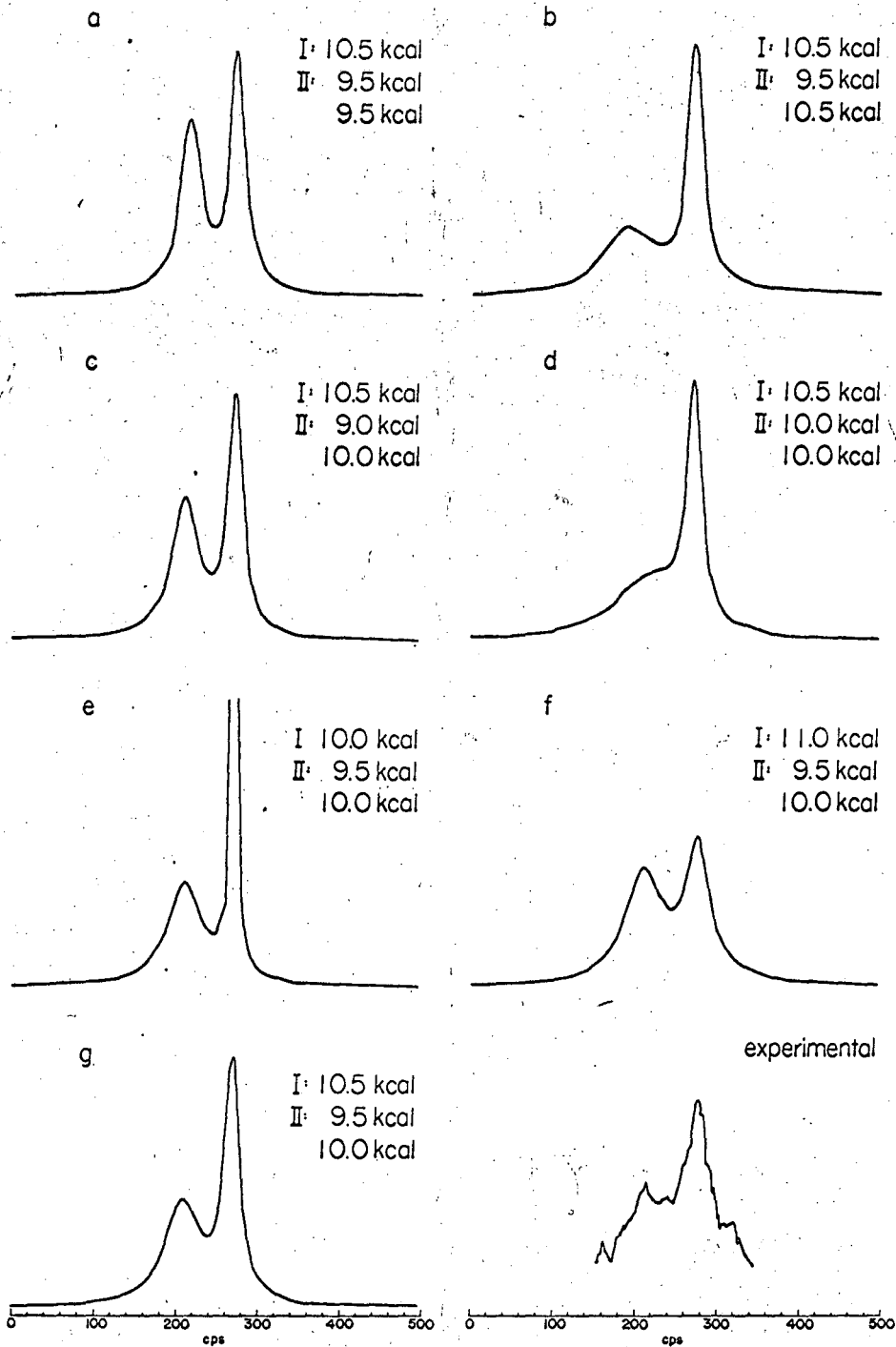
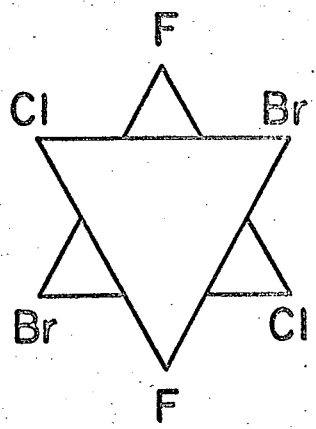
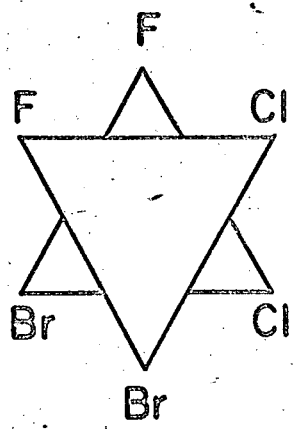


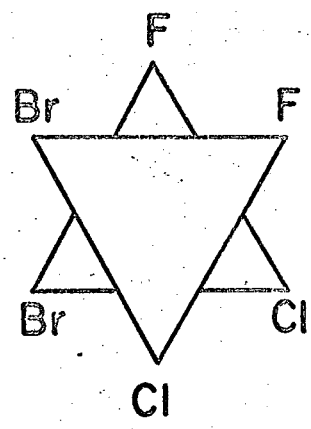
Fig. 4



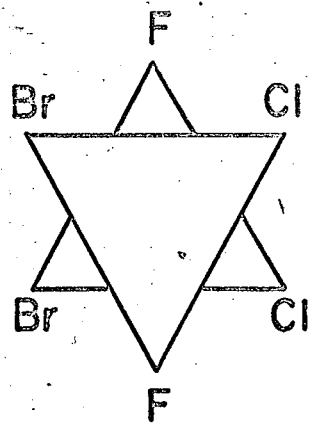
I a



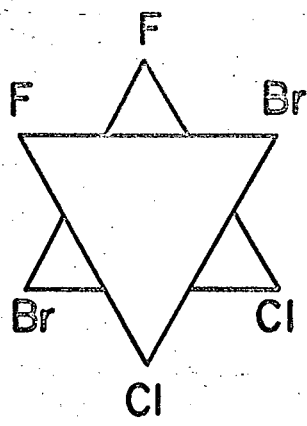
I b



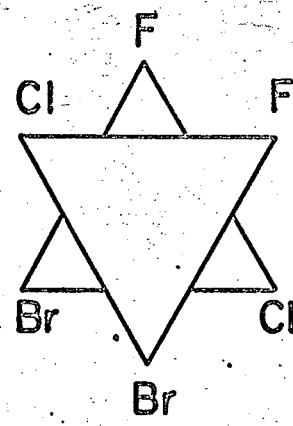
I c



II a



II b



II c

Fig. 5

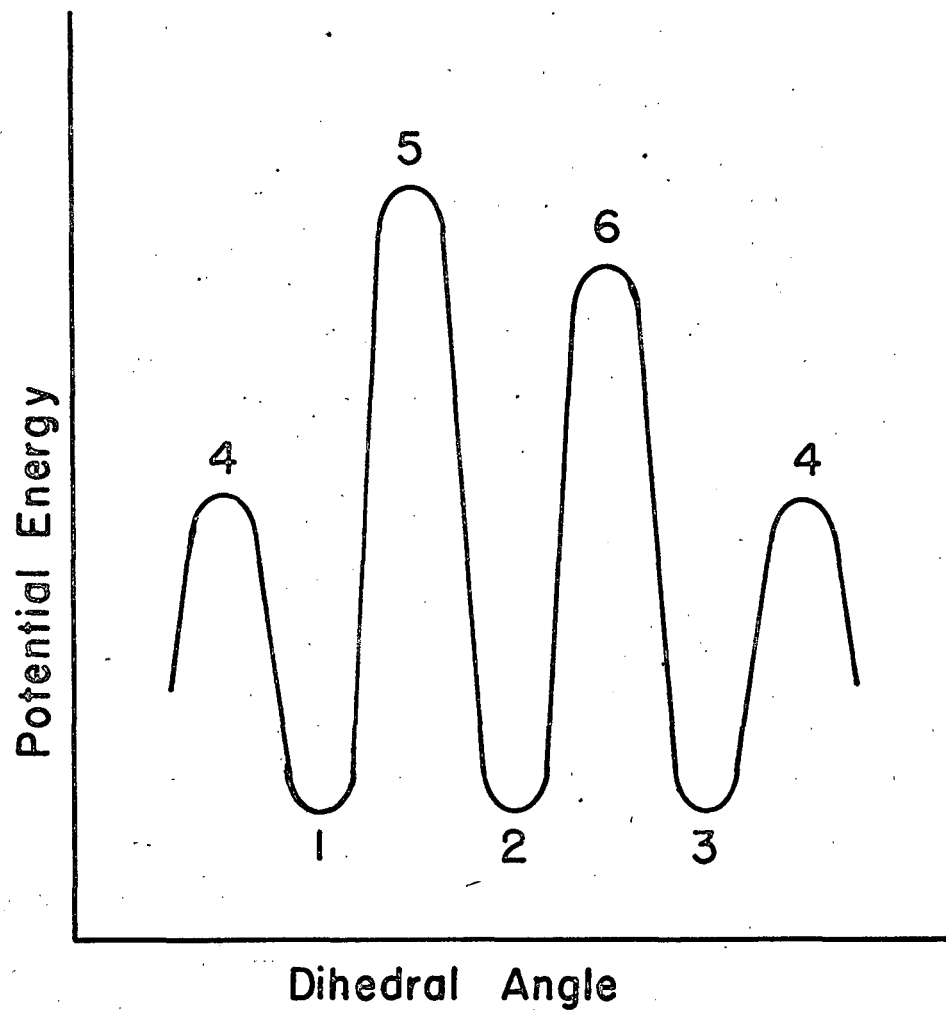


Fig. 6

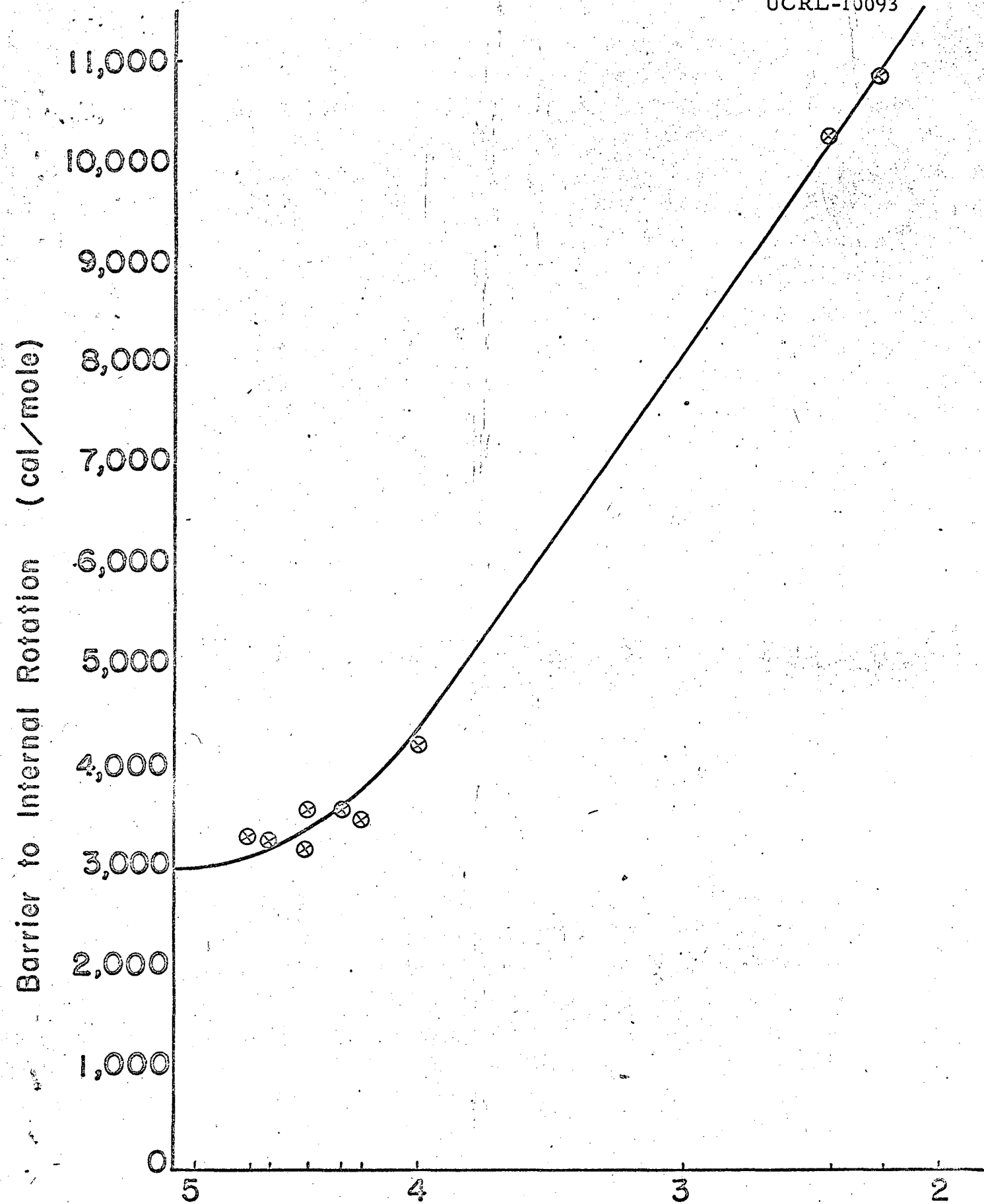


Fig. 7

$$\sum_{i=1}^6 \Delta_i$$

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.