structure, an increase of the binding to these active centers and a concomitant weaker adsorption on to the polypeptide skeleton and finally at higher pressures a multimolecular adsorption equivalent to solvation and eventually leading to solution.

If now the swelling process is not reversible, this would account for the hysteresis and if the co-operative action of the swelling should have affected principally the binding by the free basic groups then the constancy of the hysteresis would also be accounted for. Such a hypothesis appears at present to be quite reasonable and consistent with all of the known facts on the sorption process.

Los Angeles, Calif.

[DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE, NAGOYA UNIVERSITY]

On the Heats of Formation and Potential Barriers for the Internal Rotation in Hydrocarbon Molecules

BY KAZUO ITO

It has been assumed that intramolecular potential is expressible as the sum of interatomic bonding energies and inter-non-bonding atomic potential energies. On this assumption, it has been shown that the following facts can be explained very satisfactorily: (1) the regularity and irregularity of the heats of formation in paraffins and, in general, those in homologous series; (2) the difference between the heat of formation of isobutane and that of n-butane; (3) the heats of formation of cyclohexane series; (4) the heats of formation of cyclopentane series; (5) the relation between the heats of formation of decalin isomers and their molecular structures; (6) energy differences between rotational isomers in paraffin hydrocarbons; (7) the relations between the values of hindering barrier in paraffin series; and (8) the correlations between heats of formation and hindering barriers. From these results the author has concluded that both the origin of the irregularity of heats of formation and the origin of the hindering barriers in hydrocarbons are due mainly to the interactions between non-bonding atoms in a molecule.

The heats of formation of simple organic compounds can be expressed approximately by the sum of interatomic bonding energies. Although this rule is fairly extensive, Rossini and his co-workers[1] have shown that this additivity rule fails for the members below propane in paraffin hydrocarbons and, moreover, the heats of formation of iso-compounds are larger than those of the corresponding normal compounds. Rossini[2] has explained these results with the assumption that the bonding energies of C–C and C–H bonds depend upon the class of carbon atom to which these bonds are attached, but no satisfactory explanation has yet been given for the energy differences between isomers. On the other hand, many investigators have established, mainly on the basis of Raman spectrum and heat capacity measurement, the existence of rotational isomers and have estimated the energy differences and hindering barriers for their transitions. The heat of formation, energy difference between rotational isomers and the hindering barrier of transition between the corresponding isomers are all related to the intramolecular potential and should be explained on common basis although as yet no such extensive treatment has been given.

To explain these experimental results, the following assumptions were made for the intramolecular potential: intramolecular potential can be expressed by the sum of interatomic bonding energies and inter-non-bonding atomic potential energies. The interatomic bonding energy is constant regardless of the class of carbon atom. For example the heat of formation of methane, (C_1), is expressed by the sum of the six H–H interaction terms $6J_{H-H}$ and the four C–H bonding energy terms $4Q_{C-H}$

$$(C_1) = 4Q_{C-H} + 6J_{H-H}$$

In Table I the analogous equations for the heats of formation are given for the members of paraffin series, where each radical in a molecule is postulated to have the staggered configuration. Q is the bonding energy and J is the interaction of the non-bonding atoms attached to the same carbon atom. The interaction between the atoms attached to a given carbon atom and the atom attached to the nth carbon atom from the given carbon atom along the carbon skeleton in *trans* form is designated as $n$gg, $n$gg', $n$tt, $n$gt and $n$tg where g, g' and t specifies the position of an atom relative to the plane of carbon skeleton in *trans* form. g means the position of an atom above this plane, g' the position below it, and t the position on it. For examples, 3 ggHH means in propane the interaction between the two nearest H's belonging to another methyl radical with each other and 4 ttHH in n-butane means (assumed as a straight form) the interaction between the farthest hydrogen atoms attached to another terminal methyl radical with each other (in Table I this term is neglected). The term 2 gg $CH_3–CH_3(HH)$ in 2-methylbutane means the H–H interaction between two methyl groups in 2 gg position (gauche position in ethane) and contains nine terms in all. Members higher than C_4 have more terms than those contained in Table I but all interactions across greater distances are neglected. Since a real molecule has not always the tetrahedral bond angles, the interactions between the same relative positions in ideal molecules used in Table I, bond angles of which are all the tetrahedral angles, are not always the same to one another in real molecules. Hence, in order to make the expression in Table I valid, the molecules should be corrected to the ideal molecules, which are constructed with the tetrahedral bond angles. As for the energy necessary to correct a real molecule to an ideal molecule, it was assumed that it has a proper value for $-CH_3$, $-CH_2$ and $-CH$

(1) F. D. Rossini, *Chem. Revs.*, **27**, 1 (1940).

(2) F. D. Rossini, *J. Research Natl. Bur. Standards*, **13**, 21 (1934).

radicals, respectively, and these are expressed as ΔCH_3, ΔCH_2 and ΔCH. These terms, as will be shown later, have merely a significance of corrections. Since this type of correction is inadequate for higher members, the difference of heats of formation between simpler molecules similar in model to those higher members was used in the calculation for higher members to minimize the correction terms and satisfactory results were obtained. The values of heats of formation used are those[3] at 0°K. unless stated otherwise and the standard state is based on reference 4.

I. Additivity of Heats of Formation in Homologous Series.—The heats of formation in homologous series X–R (R denote an alkyl group) have, in general, a constant increment per $-CH_2$ radical for R's above propyl or butyl radical regardless of the kind of X but not for the first few members in the series. This anomaly depends also on the kind of X.

In the case of X $= -CH_3$, the increments of heats of formation per $-CH_2$ radical can be expressed as in Table II by use of Table I where (C_1) and (C_2) mean the heats of formation of CH_4 and C_2H_6, respectively. As shown in the table, the increments per $-CH_2$ are not exactly constant for the first few members and these values converge to a constant value for higher members. For R's above propyl or butyl radical the increments may be considered to be nearly constant. Since the above discussion holds for an arbitrary X, additivity of heats of formation in the other homologous series and its deviation for lower members can be explained in the same manner.

II. Heats of Formation of Iso-compounds.—The formulas in Table I are not independent of each other, i.e. some of them can be derived from others. For example (except the correction terms ΔCH_3, ΔCH_2 and ΔCH)

$$(i\text{-}C_4) = (C_1) - 3(C_2) + 3(C_3) = -24.91 \text{ kcal./mole}$$
$$\text{obsd. } -24.59 \text{ kcal./mole,}[3] \; H°_0 \text{ of } n\text{-butane} = -23.32$$

$$(\text{neo-}C_5) = 3(C_1) - 8(C_2) + 6(C_3) = -32.77 \text{ kcal./mole}$$
$$\text{obsd. } -31.16 \text{ kcal./mole,}[3] \; H°_0 \text{ of } n\text{-pentane} = -27.12$$

where $(i\text{-}C_4)$, $(\text{neo-}C_5)$, (C_1), (C_2) and (C_3) denote the heats of formation of isobutane, neopentane, methane, ethane and propane, respectively. As shown in the above formulas the stability of isobutane and neopentane compared with n-butane and n-pentane can be explained adequately by considering the interaction between non-bonding atoms. The differences between the calculated and observed values for $(i\text{-}C_4)$ and $(\text{neo-}C_5)$ may be due mainly to the deviation of a real molecule from an idealized one. Then, considering the heats of formation corrected for ΔCH_3, ΔCH_2 and ΔCH in Table I, the two equations can be obtained.

$$2\Delta CH_3 - 2\Delta CH = -0.97$$

$$3\Delta CH_3 - 3\Delta CH_2 + \Delta CH = -0.32 \text{ kcal./mole}$$

These correction equations were used in nearly all of the following calculations and the application of these corrections gave better results though it did not affect essential features. It is also possible to consider these equations as the corrections for the variation of bonding energy due to the class of carbon. The results obtained for other iso-paraffins with the same treatment are given in Table III. The agreement between calculated and observed values is satisfactory. Formulas used in calculations are given in Table IV. The heats of formation of chloro derivatives of methane and ethane can be calculated in a similar way but they are all omitted because of the large errors in experimental values.

III. Heats of Formation of Cyclohexane and Its Alkyl Derivatives.—The heats of formation of cyclohexane and its alkyl derivatives can be calculated by the same method as II using the table similar to Table I. Cyclohexane was treated as having a boat form because it has recently been shown by electron diffraction method[5] that the most part of

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TABLE I

HEATS OF FORMATION OF PARAFFIN HYDROCARBONS EXPRESSED BY THE SUM OF BONDING AND NON-BONDING ENERGY TERMS

	$\Delta H°_0$ kcal./mole	CH [Q]	CC	HH	HC [J]
CH₄	15.98	4		6	
C₂H₆	16.52	6	1	6	6
C₃H₈	19.50	8	2	7	10
C₄H₁₀	23.32	10	3	8	14
C₅H₁₂	27.12	12	4	9	18
C₆H₁₄	31.16	14	5	10	22
C₇H₁₆	35.28	16	6	11	26
Isobutane	24.59	10	3	9	12
Neopentane	31.16	12	4	12	12
2-Methylbutane	28.54	12	4	10	16
2,2-Dimethylbutane	34.7	14	5	13	16
n-Butane (gauche)		10	3	8	14
2-Methylbutane (gauche)		12	4	10	16
ΔE (n-butane)					

(3) K. S. Pitzer *Chem. Revs.*, **27**, 39 (1940).

(4) P. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Res. Natl. Bur. Standards*, **34**, 143 (1945).

(5) O. Hassel, *Tids. Kjemi Bergvesen Met.*, **3**, 32 (1943).

TABLE II
DIFFERENCES BETWEEN HEATS OF FORMATION OF PARAFFIN HYDROCARBONS

	Kcal./mole	Q		J			2gg			2tt			3gg		3gg'		3gt		3tg		3tt		2gg CH₃-CH₃	Δ		
		CH	CC	HH	HC	CC	HH	HC	CC	HH	HC	CC	HH	HC	HH	HC	HH	HC	HC	HH	HC	CC	HH	CH₃	CH₂	CH
(C₂-C₁)	-0.54	2	1	6			6			3																2	
(C₃-C₂)	-2.97	2	1	1	4		1	2	4	1	2		2		2		4			1						1
(C₄-C₃)	-3.83	2	1	1	4		1	2	4	2		1	2		2		4		-1	2						1
(C₅-C₄)	-3.80	2	1	1	4		1	2	4	2			2		2		4			1						1
(C₆-C₅)	-4.04	2	1	1	4		1	2	4			1	2		2		4			1						1
(C₇-C₆)	-4.12	2	1	1	4		1	2	4	2		1	2		2		4			1						1

TABLE III
CALCULATED VALUES OF HEATS OF FORMATION OF ISO-PARAFFIN HYDROCARBONS

	Calcd. kcal./mole Uncor.	Cor.	Obsd. kcal./mole
Isobutane	-24.91	-24.59	-24.59[1,3]
Neopentane	-32.77	-31.16	-31.16[1,3]
2-Methylpentane	-31.7	-32.2	-32.3[3,18]
3-Methylpentane	-30.6	-31.9	-31.6[3,18]
3,3-Dimethylpentane	-37.4	-37.7	-37.7[3,16]
3-Methylhexane	-35.6	-35.6	-35.2[3,16]
2-Methylbutane	-27.8	-28.3	-28.5[3]

TABLE IV
FORMULAS USED TO CALCULATE THE HEATS OF FORMATION OF ISOPARAFFIN HYDROCARBONS

$(i\text{-}C_4)O(C_1) - 3(C_2) + 3(C_3)$

$(neo\text{-}C_5) = 3(C_1) - 8(C_2) + 6(C_3)$

$(2\text{-Methyl-}C_5) = 0.5(2,2\text{-dimethyl-}C_5) + 0.5(C_5) - 0.5 \cdot (C_3) + (C_2) - 0.5(C_1)$

$(3\text{-Methyl-}C_5) = (C_5) + (2,2\text{-dimethyl-}C_4) - (C_4) - 3 \cdot (C_3) + 5(C_2) - 2(C_1)$

$(3,3\text{-Dimethyl-}C_5) = (3\text{-methyl-}C_5) + (2,2\text{-dimethyl-}C_4) - (C_4) - 2(C_3) + (C_2) - (C_1)$

$(3\text{-Methyl-}C_6) = (3\text{-methyl-}C_5) + (2\text{-methyl-}C_5) - (2 \cdot methyl\text{-}C_4) + (C_6) - 2(C_5) + (C_4)$

$(2\text{-Methyl-}C_4) = 0.5(2,2\text{-dimethyl-}C_4) + 0.5(C_4) - 0.5 \cdot (C_3) + (C_2) - 0.5(C_1)$

cyclohexane has a boat form at room temperature. For example, the heat of formation of cyclohexane can be expressed as follows, using those of diamond and paraffin hydrocarbons

$(cyclohexane) = (diamond)/2 + 6(2\text{-methyl-}C_4) - 3(2,2\text{-}dimethyl\text{-}C_4) - 3(C_5) + 9(C_3) - 10(C_2) + 3(C_1)/2 =$

-19.97 ($\theta_D = 2230°K.$)

-20.97 ($\theta_D = 2500°K.$)

obsd. -20.01 kcal./mole[6]

The correction equations in II were used in this calculation. As diamond is solid, heat of formation at 0°K. and the correction for zero point energy were used to cancel the difference between the solid and gaseous state. Debye temperature θ_D was estimated from the references.[7,8] It is interesting that the heat of formation of a gaseous molecule can be calculated from that of solid molecule. Similarly, the heats of formation of methylcyclohexane, ethylcyclohexane and seven dimethylcyclohexanes can be calculated. The results obtained are given in Table V and formulas used are given in Table VI. The structural models of isomers were taken from the paper by Beckett and his co-workers.[9] The calculated and observed[6] values agree with each other very well. The differences between the heats of formation of six dimethylcyclohexanes, except 1,1-dimethyl-

(6) J. E. Kilpatrick, H. G. Werner, C. W. Beckett, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **39**, 523 (1947).

(7) R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge University Press, p. 149.

(8) K. S. Pitzer, *J. Chem. Phys.*, **6**, 68 (1938).

(9) C. W. Beckett, K. S. Pitzer and R. S. Spitzer, THIS JOURNAL, **69**, 2488 (1947).

cyclohexane, can also be approximated[8] by the integral multiple of the energy difference between *trans* and gauche forms of *n*-butane or of *n*-pentane.

TABLE V
CALCULATED VALUES OF HEATS OF FORMATION OF CYCLO-HEXANE AND ITS METHYL, ETHYL AND DIMETHYL DERIVATIVES
Where *c* is *cis*, *t* is *trans*, D is dimethylcyclohexane

	Calcd. kcal./mole	Obsd.[6] kcal./mole
Cyclohexane	$-19.97(\theta_D = 2230)$	-20.01
	$-20.27(\theta_D = 2500)$	
(Methylcyclohexane) − (cyclohexane)	-6.77	-6.31
(Ethylcyclohexane) − (methylcyclohexane)	-3.04	-2.64
$(c\text{-}1,4\text{-D}) - (1,1\text{-D})$	0.94	0.85
$(c\text{-}1,4\text{-D}) - (c\text{-}1,2\text{-D})$	-1.30	-1.13
$(c\text{-}1,4\text{-D}) - (t\text{-}1,2\text{-D})$	0.88	0.83
$(c\text{-}1,4\text{-D}) - (c\text{-}1,3\text{-D})$	1.93	1.94
$(c\text{-}1,4\text{-D}) - (t\text{-}1,3\text{-D})$	-0.03	-0.02
$(c\text{-}1,4\text{-D}) - (t\text{-}1,4\text{-D})$	1.82	1.91
$(c\text{-}1,4\text{-D})\text{-}(ethylcyclohexane)$	-1.03	-1.14

TABLE VI
FORMULAS USED TO CALCULATE THE HEATS OF FORMATION OF CYCLOHEXANE AND ITS METHYL, ETHYL AND DIMETHYL DERIVATIVES
Where *c* is *cis*, *t* is *trans*, D is dimethylcyclohexane

$(Cyclohexane) = 0.5(diamond) - 3(2,2\text{-dimethyl-}C_4) + 6(2\text{-methyl-}C_4) - 3(C_5) + 9(C_3) - 10(C_2) + 1.5(C_1)$

$(Methylcyclohexane) - (cyclohexane) = (i\text{-}C_4) + 2(C_4) - 5(C_3) + 2(C_2)$

$(Ethylcyclohexane) - (methylcyclohexane) = (3\text{-methyl-}C_5) - (2\text{-methyl-}C_4) - (C_5) + 2C(C_4) - (C_3)$

$(c\text{-}1,4\text{-D}) - (1,1\text{-D}) = 2(2\text{-methyl-}C_4) - (2,2\text{-dimethyl-}C_4) - (C_4)$

$(c\text{-}1,4\text{-D}) - (c\text{-}1,2\text{-D}) = -2(2,2\text{-dimethyl}\cdot C_4) + 4(2\text{-methyl-}C_4) - (2\text{-methyl-}C_5) + 3(C_3) - 7(C_2) + 3(C_1)$

$(c\text{-}1,4\text{-D}) - (t\text{-}1,2\text{-D}) = (2\text{-methyl-}C_5) - 2(2,2\text{-dimethyl-}C_4) + 4(2\text{-methyl-}C_4) + 5(C_3) - 3(C_2) + (C_1)$

$(c\text{-}1,4\text{-D}) - (c\text{-}1,3\text{-D}) = -(C_5) + 2(C_4) - (C_3)$

$(c\text{-}1,4D) - (t\text{-}1,3D) = -(2\text{-methyl-}C_5) + (2\text{-methyl-}C_4) + (C_5) - (C_4)$

$(c\text{-}1,4\text{-D}) - (t\text{-}1,4D) = 2(2\text{-methyl-}C_4) + 2(C_5) - 8(C_4) + 2(C_3) + 4(C_2) - 2(C_1)$

$(c\text{-}1,4\text{-D}) - (ethylcyclohexane) = -(2\text{-methyl-}C_5) + 2(2\text{-methyl-}C_4) + 2(C_5) - 5(C_4) + 2(C_3)$

IV. Heats of Formation of Cyclopentane Alkyl Derivatives.—The results obtained on the heats of formation of methyl-, 1,1-dimethyl-, *t*-1,2-dimethyl- and *t*-1,3-dimethylcyclopentane are given in Table VII. The formulas used are given in Table VIII. The correction equations in II were used. Here, the cyclopentane ring was treated as having a regular pentagon form and the energy necessary to correct the real molecule to this pentagon form was con-

sidered to be equal on each side of the equation used in the calculation. The heat of formation of cis-1,2-dimethyl-cyclopentane will be used later to calculate the hindering barrier in n-butane.

TABLE VII

CALCULATED VALUES OF HEATS OF FORMATION OF METHYL-
AND DIMETHYLCYCLOPENTANES

	Calcd. kcal./mole	Obsd.[6,9] kcal./mole
Methylcyclopentane	−16.5	−16.62
1,1-Dimethylcyclopentane	−33.44	−33.05
t-1,3-Dimethylcyclopentane	−32.54	−32.67

TABLE VIII

FORMULAS USED TO CALCULATE THE HEATS OF FORMATION
OF METHYL- AND DIMETHYLCYCLOPENTANES

Where d is dimethylcyclopentane, H.B. is hindering barrier

(Methylcyclopentane) = (cyclopentane) + 2(C_3) − 3(C_2) +
(C$_1$) − 2(H.B. or C_3H_8) + 2(H.B. of C_2H_6) + 2(t-1,2-
d) − 2(t-1,3-d)

(1,1-d) = 2(methylcyclopentane) − (cyclopentane) −
2(2-methyl-C_4) + (2,2-dimethyl-C_4) + (C_4)

(t-1,3-d) = 2(methylcyclopentane) − (cyclopentane)

V. Heats of Formation and Molecular Structures of Decalin Isomers.—Hitherto the molecular structures of the trans and cis isomers of decalin have tacitly been considered as a chair form I and a boat form I in Fig. 2. From the present knowledge, however, the boat form I seems to be very unstable. Davis and Gilbert[10] showed, in fact, that the heat of isomerization is only 2.12 kcal./mole in liquid state at 25°. Bastiansen and Hassel[11] concluded from electron diffraction experiments that cis-decalin has a chair form II. The present author has treated these molecules by the same method as used above.

The possible geometrical models[12] of decalin are shown in Fig. 1. The chair forms I and II consist of the two chair form molecules of cyclohexane combined with each other while mixed form I, II and III consists of a chair and a boat form of cyclohexane. The results calculated for the chair form I and II and boat form I are given in Table IX. Formulas used are given in Table X. The correction formulas in II were also used in these cases and the energy difference 5.6 kcal./mole between the chair and boat form of cyclo-

TABLE IX

HEATS OF FORMATION AND ISOMERIZATION OF DECALIN
ISOMERS

	Calcd. kcal./mole (25°)		Obsd.[10,13] kcal./ mole (25°)
Chair form I	−46.8	t-decalin	−46.7
(Chair form I) −	− 1.6	(t-decalin) −	− 1.2
(Chair form II)		(c-decalin)	
(Chair form I) −			
(Boat form I)	− 9.1		

TABLE X

FORMULAS USED TO CALCULATE THE HEATS OF FORMATION
AND ISOMERIZATION OF DECALIN ISOMERS

(Chair form I) = 2(cyclohexane) + 6(C_4)(trans) − 10
(C$_3$) + (C$_2$) + 2(C$_1$)

(Chair form I) − (chair form II) = −3(2-methyl-C_4)
(trans form) + 6(C_4)(trans form) − 6(C_2) + 3(C_1)

(Chair form I) − (boat form I) = 2(cyclohexane, chair
form) − 2(cyclohexane, beat form) − (methylcyclo-
pentane) + (cyclopentane) − 2(H.P. of C_3H_8) + (H.B.
of C_2H_6) − 2(2,2-dimethyl-C_4) + 4(2-methyl-C_4) −
5(C_2) + 3(C_1)

(10) D. F. Davies and E. C. Gilbert, THIS JOURNAL, **63**, 1586 (1941).
(11) O. Bastiansen and O. Hassel, Nature, **157**, 765 (1946).
(12) W. A. Wightman, J. Chem. Soc., **127**, 1421 (1925).

hexane was taken from the literature.[8] The energy differences used for the rotational isomers of-2-methylbutane and n-butane are 1200 and 800 cal./mole, respectively. The heat of vaporization was estimated from the literature.[13] As shown in Table IX, the observed heat of formation of trans-decalin agrees well with the calculated value of chair form I and the observed heat of isomerization agrees with the difference between the calculated heats of formation of chair form I and II. The heat of isomerization between chair form I and boat form I does not agree with the observed heat of isomerization exactly. Considering the above results, the boat form II will be less stable by 2 ∼ 3 kcal./ mole compared with the boat form I and the mixed form I, II and III by more than 4 ∼ 6 kcal. in comparison to the chair form I. Then, the structures of trans- and cis-decalin can be concluded as follows: trans-decalin has the structure of chair form I while cis-decalin chair form II. This conclusion agrees with the results of Bastiansen and Hassel[11] and Inamura,[14] who obtained the same results from the study on Raman spectra.
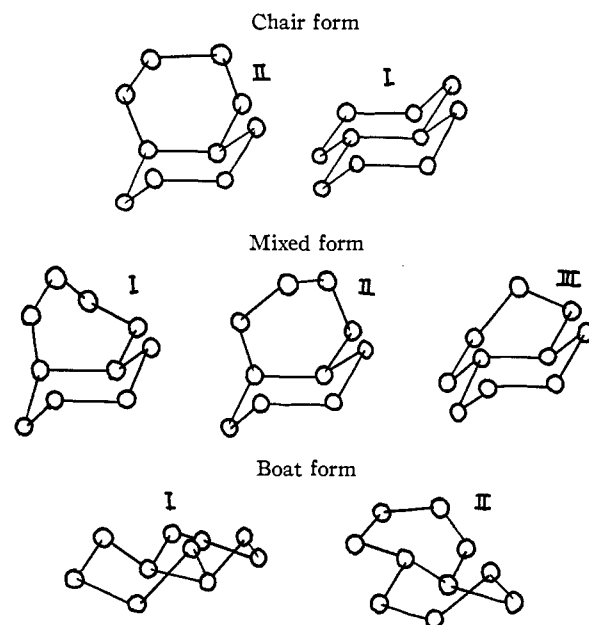
Chair form

Mixed form

Boat form

Fig. 1.—The possible geometrical models of decalin isomers.

VI. The Energy Differences between Rotational Isomers. —Since the energy difference between two rotational isomers can be considered as the difference between the heats of formation of two rotational isomers, the energy difference between rotational isomers can be estimated by comparison of the calculated heat of formation of one of the two isomers with the observed heat of formation corrected to 0°K. if the heat of formation of one of the two rotational isomers could be calculated. For example, as shown in Table I, the energy difference between the trans and gauche form (cf. Fig. 2) of n-butane can be expressed, using the heats of formation of other substances, as

(trans form) − (gauche form) = 2(C_4) − 2(2 methyl-
C$_4$) + (C$_1$) − 2(C_2) = −0.7 kcal./mole

If the correction formulas in II are not used, the value of this equation is −1.05 kcal./mole. If the heats of formation of 2,2-dimethylbutane and other substances are used instead of (2-methyl-C_4) on the right hand side of the equation, the value of the equation becomes −1.0 kcal./mole, but the use of (2-methyl-C_4) is more appropriate to cancel the correction terms due to the deviation of the real molecule from the ideal molecule than the use of (2,2-dimethyl-C_4) and others because the gauche form of n-butane and the trans form of 2-methylbutane are similar in their models as shown in Fig. 1. The heat content of 2-methylbutane at standard state taken from the literature[8] was calculated by use of

(13) W. F. Seyer and C. W. Mann, THIS JOURNAL, **67**, 328 (1945).
(14) Y. Inamura. Kagaku (Japan, in Japanese). **19**, 59 (1942).

1600 cal./mole for the energy difference between the rotational isomers of 2-methylbutne, but the change of the value calculated above (−0.7 or −1.05 kcal./mole) due to the variation of 1600 cal./mole from 0 to 1600 cal./mole is less than 100 cal./mole. The value of 0.7 kcal./mole obtained above agrees very well with the value of 0.8 kcal./mole obtained by Pitzer.[3] The values of the energy difference between the rotational isomers of n-pentane, 2,3-dimethylbutane, 2-methylbutane and 2,3-dimethylpentane calculated in the same way are given in Table XI. Formulas used are in Table XII. The stable and unstable forms of these substances are shown in Fig. 2. The result of 2,3-dimethylbutane is interesting because the gauche form is more stable than the *trans* form in this molecule by an amount 1500 cal./mole in contradiction to the case of many other molecules in agreement with the result of Sheppard and Szasz.[15,16] The gauche form of 2,3-dimethylpentane is more stable than the *trans* form by 1100 cal./mole. In order to minimize errors due to the deviation from an ideal molecule, (2,2-dimethyl-C$_4$), (2,2,3-trimethyl-C$_4$) and (2,3-dimethyl-C$_4$) (*trans* form) were used in Table XII to calculate (2-methyl-C$_4$) (gauche), (2,3-dimethyl-C$_4$) and (2,3-dimethyl-C$_5$), respectively.

| *trans* | gauche | *trans* | gauche |
| n-butane | | n-pentane | |

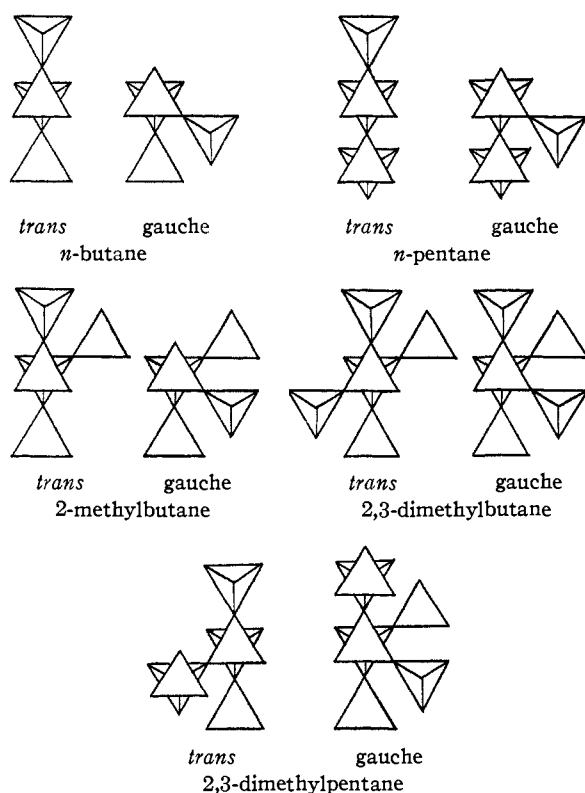| *trans* | gauche | *trans* | gauche |
| 2-methylbutane | | 2,3-dimethylbutane | |

| *trans* | gauche |
| 2,3-dimethylpentane | |

Fig. 2.—The configurations of rotational isomers.

The energy differences between the rotational isomers of Cl derivatives of ethane can also be treated in a similar manner but they are not discussed here due to the large errors in experimental data.

TABLE XI

CALCULATED VALUES OF ENERGY DIFFERENCES BETWEEN THE ISOMERS OF PARAFFIN HYDROCARBONS

| | Energy difference, kcal./mole | |
	Uncor.	Cor.
n-Butane	1.0	0.7
n-Pentane	1.1	0.8
2-Methylbutane	2.5	1.2
2,3-Dimethylbutane	1.3	1.5
2,3-Dimethylpentane	1.3	1.1

(15) N. Sheppard and G. J. Szasz, J. Chem. Phys., **17**, 86 (1949).
(16) G. F. Davis and E. C. Gilbert, THIS JOURNAL, **63**, 2730 (1941).

TABLE XII

FORMULAS USED TO CALCULATE THE ENERGY DIFFERENCES BETWEEN THE ISOMERS OF PARAFFIN HYDROCARBONS

ΔE of n-butane = $2(C_4) - (2\text{-methyl-}C_4)^3 - 2(C_2) + (C_1)$

ΔE of n-pentane = $2(C_5) - (2\text{-methyl-}C_5)^3 - (C_4) + (C_3) - 2(C_2) + (C_1)$

2-Methylbutane(gauche) = $(2,2\text{-dimethyl-}C_4)^3 - (C_4) - (C_3) + 4(C_2) - 2(C_1)$

2,3-Dimethylbutane(*trans*) = $(2,2,3\text{-trimethyl-}C_4)^{15\,3} - (2,2\text{-dimethyl-}C_4) + (C_4) + 2(C_3) - 3(C_2) + (C_1)$

2,3-Dimethylpentane(*trans*) = $(2,3\text{-dimethyl-}C_4)(trans) + (2\text{-methyl-}C_5) - (C_4) - 2(C_3) + 3(C_2) - (C_1)$

VII. Relations between Hindering Barriers of Methyl Radicals.—The value of the hindering barrier of a given methyl group in a molecule can be considered to be equal to the difference of heats of formation between the molecule in which all methyl groups are in staggered configuration and the hypothetical molecule in which the given methyl group is in eclipsed configuration. Then, the relations between the hindering barriers of methyl groups can be calculated by the same method as used in I $\sim$ VI for the heats of formation. The results obtained by this treatment are

Hindering barrier of isobutane = 2(H.B. of propane) − (H.B. of ethane) = 2 × 3.30 − 2.75 = 3.85 kcal./mole

obsd. 3.85 kcal./mole[17]

Hindering barrier of neopentane = 3(H.B. of propane) − (H.B. of ethane) = 3 × 3.30 − 2 × 2.75 = 4.40 kcal./mole

obsd. 4.5 kcal./mole[17]

The results obtained for the hindering barriers of branched methyl groups are given in Table XIII. Formulas used are given in Table XIV, where the value 3400 cal./mole has been used for the hindering barrier of −CH$_3$ in n-butane.

TABLE XIII

CALCULATED VALUES OF HINDERING BARRIERS FOR METHYL GROUPS

Where H.B. is hindering barrier

	Calcd. cal./mole	Obsd. cal./mole
Isobutane	3850	3850[17]
Neopentane	4400	4500[17]
−CH$_3$ of 2-methylbutane at 1st carbon	3950	
−CH$_3$ of 2-methylbutane at 4th carbon	(H.B. of branched −CH$_3$ of 2-methylbutane) − 450	
−CH$_3$ of 2,2-dimethylbutane at 4th carbon	(H.B. of branched −CH$_3$ of 2,2-dimethylbutane) − 800	
−CH$_3$ of 2,2-dimethylbutane at 2nd carbon	(H.B. of branched −CH$_3$ of 2-methylbutane) + 350	
−CH$_3$ of 2,2-dimethylbutane at 1st carbon	4300	

VIII. Relations between the Heats of Formation and the Hindering Barriers of Methyl Groups.—As shown above the values of the heats of formation and the hindering barriers of methyl groups can be explained on a common basis. The hindering barriers can be calculated, furthermore, by use of the heats of formation of cyclopentane series because −CH$_2$ groups in cyclopentane ring are in eclipsed configuration to one another. The results obtained are as follows: the higher hindering barrier of the rotating ethyl group in n-butane = 6.10 kcal./mole, the lower hindering barrier of the rotating ethyl group in n-butane = 3.72 kcal./mole and the hindering barrier of the branched methyl group in 2-methylbutane = 3.51 kcal./mole where the heats of formation at 25° were used for all and the value 800 cal./mole was used

(17) J. G. Aston and G. H. Messerly, *ibid.*, **58**, 2354 (1936); K. S. Pitzer, *J. Chem. Phys.*, **5**, 473 (1937).

TABLE XIV

FORMULAS USED TO CALCULATE THE HINDERING BARRIERS
OF METHYL GROUPS

Where H.B. is hindering barrier

(H.B. of isobutane) = 2(H.B. of propane) − (H.B. of ethane)

(H.B. of neopentane) = 3(H.B. of propane) − 2(H.B. of ethane)

(H.B. of 2-methylbutane at 1st carbon) = (H.B. of isobutane) + (H.B. of n-butane) − (H.B. of propane)

(H.B. of 2,2-dimethylbutane at 1st carbon) = (H.B. of neopentane) + (H.B. of n-butane) − (H.B. of propane)

(H.B. of 2-methylbutane at 4th carbon) = (H.B. of branched methyl radical of 2-methylbutane) + (H.B. of n-butane) − (H.B. of isobutane)

(H.B. of 2,2-dimethylbutane at 4th carbon) = (H.B. of branched methyl radical of 2,2-dimethylbutane) + (H.B. of n-butane) − (H.B. of neopentane)

(H.B. of branched methyl radical of 2,2-dimethylbutane) = (H.B. of branched methyl radical of 2-methylbutane) + (H.B. of neopentane) − (H.B. of isobutane)

for the energy difference between two rotational isomers of n-butane. Formulas used are given in Table XV. Correction formulas in II were also used in these cases. Values obtained are reasonable from the present knowledge. Recently, Dailey and Felsing[18] have given the value 3.6 kcal./mole for the hindering barrier of n-butane. The combination of the results obtained in VI and VIII gives the variation of the intramolecular potential of n-butane with the rotation of ethyl group as shown in Fig. 3.

TABLE XV

FORMULAS USED TO CALCULATE THE HINDERING BARRIERS
IN n-BUTANE AND 2-METHYLBUTANE

Where H.B. is hindering barrier

(Higher hindering barrier of rotating ethyl group in n-butane) = (cis-1,2-dimethylcyclopentane) + 2(methylcyclopentane) − (cyclopentane) + 2(H.B. of propane) − (H.B. of ethane) + (C₄)(trans form) − 2(C₃) + (C₂)

(Lower hindering barrier of rotating ethyl group in n-butane) = −0.5(methylcyclopentane) + 0.5(cyclopentane) + (H.B. of propane) + (C₄)(trans form) − (C₃) − 0.5 (C₂) + 0.5(C₁)

(Hindering barrier of branched methyl group in 2-methylbutane) = −(ethylcyclopentane) + (methylcyclopentane) + (H.B. of isobutane) − (H.B. of methyl group in n-butane) + (H.B. of propane) + (2-methylbutane) − 3(C₃) + 3(C₂) − (C₁)

(18) B. P. Dailey and W. A. Felsing, THIS JOURNAL, 65, 44 (1943).

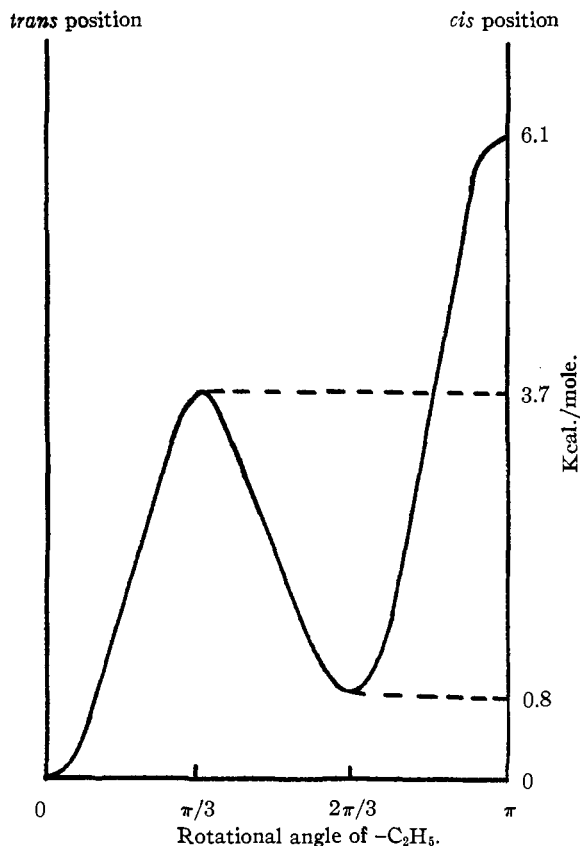*trans* position   *cis* position

Fig. 3.—The variation of the intramolecular potential of n-butane by the rotation of ethyl group.

IX. Conclusion

By analyzing the heats of formation of hydrocarbon molecules the present author concluded as follows: the regularity of heats of formation and the deviation from this regularity in homologous series, the energy difference between geometrical isomers in the case of isobutane and butane or *cis*- and *trans*-decalin, the energy difference between rotational isomers, and the hindering potential for an intramolecular rotation are all caused mainly by the interaction between non-bonding atoms, the observed values of these quantities and relations between them being explained adequately by taking into account the interaction terms between non-bonding atoms.

NEGOYA, JAPAN