Spectroscopic Studies of Rotational Isomerism. III. The Normal Paraffins in the Liquid and Solid States

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The Raman spectra of *n*-butane, *n*-pentane, *n*-hexane, and *n*-heptane have been investigated in the liquid phase between 310°K and their melting points, and also in the solid phase. The room temperature spectra clearly show the presence of appreciable concentrations of two rotational isomers in butane and pentane, and of three isomers in hexane and probably in heptane. In the solid phase only one of these isomers is present, and in agreement with previous conclusions based on spectroscopic and other evidence, this lowest energy form was assumed to possess the planar, *trans-*, zig-zag configuration. The spectra of the solids yield experimental values for the limiting skeletal stretching frequencies of the zig-zag form, and these were compared with values calculated by previously established methods. The photoelectric spectrograph was used for quantitative intensity measurements on selected line pairs of each molecule over appropriate temperature intervals, and from the results values were obtained for the energy difference, $-\Delta H$, between rotational isomers. The values obtained were 760 ± 100 cal. mole^{-1} in *n*-butane, 450 ± 60 cal. mole^{-1} in *n*-pentane, 520 ± 70 and 470 ± 60 cal. mole^{-1} in *n*-hexane. No quantitative result could be obtained for *n*-heptane. The observed gaseous heat capacities of *n*-butane, *n*-pentane, and *n*-hexane were compared with values calculated by statistical mechanics. It was found that for *n*-pentane and *n*-hexane the calculated values do not agree accurately with the experimental results, probably because of the simplified partition functions used to obtain the compositions of the isomeric mixtures.

I. INTRODUCTION

IN the first paper of this series[1] we have shown that the photoelectric Raman spectrograph[2] recently developed in this laboratory can be applied to a quantitative study of the rotational isomers in liquid normal butane. A value was obtained for the energy difference in good agreement with that previously used by Pitzer[3] in his treatment of the thermodynamic properties of hydrocarbons. In this manner it was also possible to separate the Raman spectra of the two isomers, and thus to make a complete assignment of frequencies for the low energy, *trans*-isomer of *n*-butane. In the preceding paper[4] a simple method of obtaining the Raman spectra of solids was described, and the results obtained on the *n*-paraffins were given.

In continuation of these studies it seemed of interest to make quantitative line intensity measurements on the *n*-paraffins. It was hoped to obtain values for the numbers of isomers present and for the energy differences between them. These results, together with the spectra of the solids,[4] should enable us to assign the appropriate frequencies to the skeletal stretching modes of vibration of the different rotational isomers. The improved techniques used in this work also made a reinvestigation of *n*-butane possible, to yield a valuable independent confirmation of our previous result.

II. EXPERIMENTAL

The work on the spectra of the liquids was done essentially as described before.[1] A great improvement was introduced, however, by utilizing the low pressure Hg arcs[5] in conjunction with the photoelectric measurements. The two advantages of these sources are their low general background and the very weak satellites of the 4358A Hg exciting line. This latter property was essential for quantitative work on the 835–789-cm^{-1} line pair of *n*-butane.[1] To obtain improved resolution for this work we further narrowed the spectrograph slits. The spectra of the solid paraffins were obtained by the general crystal powder method described in the preceding paper.[4]

[1] G. J. Szasz, N. Sheppard, and D. H. Rank, J. Chem. Phys. **16**, 704 (1948).

[2] D. H. Rank and R. Wiegand, J. Opt. Soc. Am. **36**, 325 (1946).

[3] K. S. Pitzer, J. Chem. Phys. **8**, 711 (1940).

[4] D. H. Rank, N. Sheppard, and G. J. Szasz, J. Chem. Phys. **17**, 83 (1949).

[5] D. H. Rank, N. Sheppard, and G. J. Szasz, J. Chem. Phys. **16**, 698 (1948).

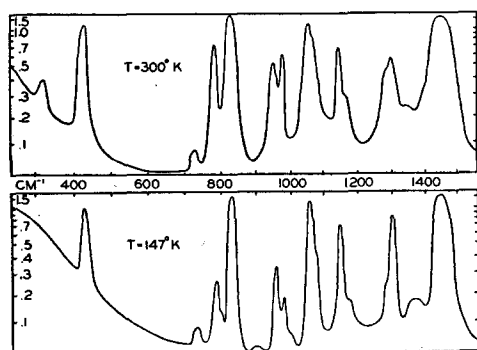Fig. 1. Smoothed microphotometer curves of the Raman spectrum of liquid n-butane at 300°K and at 147°K.

Fig. 2. Smoothed microphotometer curves of the Raman spectrum of liquid n-pentane at 300°K and at 150°K.

The normal paraffin samples were the same as used before.[1,4] They were stated to be 99+ percent pure and were used without further purification. The small amounts of water present produced slight cloudiness of the liquids below the icepoint, but because of the low background of Rayleigh scattering obtained with our sources, this did not interfere with any of the measurements.

III. THE EXPERIMENTAL RESULTS

A. The Raman Spectra

In Figs. 1–3 are shown the Raman spectra of n-butane, n-pentane, and n-hexane below 1500 cm⁻¹ in the liquid phase at the higher and lower temperatures, respectively. These have been traced from the microphotometer curves as described before. A low temperature spectrum in the liquid was not obtained with the n-heptane sample. It can be seen at once that the spectra undergo marked changes with temperature. The spectra of the solid hydrocarbons between 1500 and 600 cm⁻¹ are shown schematically in Fig. 4.[4] Although longer exposure times might bring up a few more weak lines in these spectra, the plates that we have obtained are sufficient to decide the behavior on solidification of all the strong lines in the room temperature spectra. This does not apply to frequencies below 600 cm⁻¹ because in this region the increased background obscures all but the strongest lines.

The Raman spectra of n-butane, n-pentane, n-hexane, and n-heptane are summarized in Table I. This table has been arranged in such a way as to show the similarities in these spectra. Each frequency is followed by the relative in-
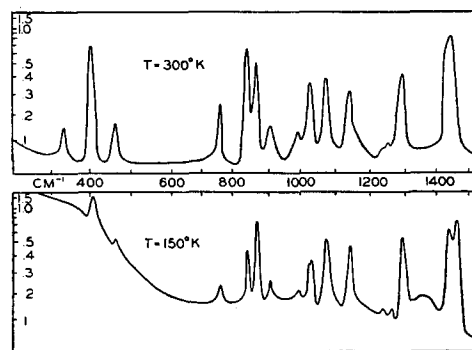
tensity of the line, and in the case of the liquid spectra by a + or − sign, indicating a relative intensity increase or decrease of the line upon cooling. The asterisk indicates that the line splits upon cooling, and that the two components behave differently. It would be expected that all the lines marked + in the liquid spectrum would persist in the solid spectrum, and this appears to be the case for most of the lines observed. Those that do not seem to obey this condition are relatively weak in the liquid spectra, and might show in the solid spectra with longer exposures.

The frequencies listed for n-butane are taken from our first paper, and for the other compounds the values given by Kohlrausch[6] have been used. In a few cases we have observed weak lines not recorded by Kohlrausch, and these frequencies have been estimated to approximately 5 cm⁻¹ by interpolation from the known values.
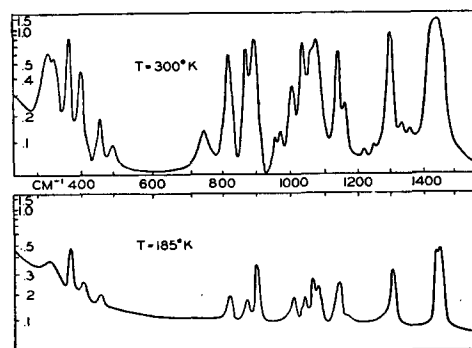

Fig. 3. Smoothed microphotometer curves of the Raman spectrum of liquid n-hexane at 300°K and at 185°K.

[6] K. W. F. Kohlrausch, "Ramanspektren," Hand und Jahrbuch der Chemischen Physik (Akademische Verlagsgesellschaft, Leipzig, 1943), p. 210.
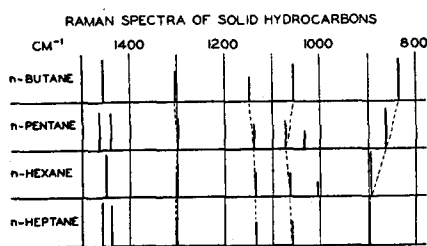
RAMAN SPECTRA OF SOLID HYDROCARBONS

FIG. 4. The Raman spectra of normal paraffins in the solid state.

B. The Determination of the Energy Difference between the Rotational Isomers

The method used to obtain the energy differences was that of Langseth and Bernstein,[7] and the equations used for the calculations were given in our previous paper.[1] In this investigation we have restricted our attention to the strong polarized lines[8] between 780–900 cm⁻¹, as in all cases cooling produced marked relative intensity changes in this region.**

The results obtained on the energy differences, $-\Delta H$, are summarized in Table II, together with

TABLE I. Observed Raman frequencies in liquid and solid n-paraffins (below 1500 cm⁻¹).

n-butane		n-pentane		n-hexane		n-heptane	
Liquid 300°K	Solid 90°K	Liquid 300°K	Solid 90°K	Liquid 300°K	Solid 90°K	Liquid 300°K	Solid 90°K
1455 (10)+	1455	1450 (10)+	{1463	1450 (10)+	1450	1450 (10)	{1457
1370 (0)			1438	1360 (0)			1438
				1337 (0)		1350? (0)	
1304 (4)+	1304	1299 (5)+	1299	1302 (7)+	1302	1302 (7)	1302
1282 (2)−							
		1260 (0)+		1265 (0)			
		1240 (0)+		1235 (0)			
1167 (1)				1165 (2)−		1161 (1)	
1148 (4)+	1148	1138 (4)+	1138	1136 (5)+	1136	1136 (4)	1136
1077 (3)−				1077 (6)−		1082 (6)	
1058 (9)+	1058	1073 (4)+	1073	1062 (4)+	1062	1060	1060
		1033 (4)*	1033	1039 (5)−		1046 (3)	
				1007 (3)+	1007	1019 (1)	
981 (4)−		995 (1)		970 (1)		951 (1)	
956 (3)+		900 (2)+		950 (1)			
835 (10)+	835	862 (6)+	862	896 (10)+	896	899 (5)	899
		837 (8)−		867 (6)−		846 (3)	
				825 (5)−		831 (5)	
789 (5)−		762 (3)−		729 (1)		772 (2)	
				500 (0)			
432 (7)+	432	463 (2)+	463	460 (1)+		494 (0)	
				400 (3)−		447 (0)	
		399 (8)+	399			396 (1)	
325 (1)−		334 (2)		363 (5)+		350 (0)	
				323 (3)−		309 (3)	
				309 (4)		280 (0)	

[7] A. Langseth and H. J. Bernstein, J. Chem. Phys. 8, 410 (1940).

[8] For detailed polarization data see Report on the Raman Spectra of Hydrocarbons (Petroleum Refining Laboratory, School of Chemistry and Physics, The Pennsylvania State College, May 1947).

** This was also observed by H. Okazaki, Bull. Chem. Soc. Japan 18, 364 (1943); Chem. Abs. 41, 4382 (1947).

the temperatures used, and the line pairs that were chosen for investigation. In the case of n-hexane two prominent lines decreased notably in intensity on going to low temperatures, and measurements were made on each of these with respect to the 896-cm⁻¹ line which did not behave in this fashion. Several measurements of the line-pair ratios were made for each substance at both the upper and the lower temperatures. The values given for $-\Delta H$ were computed from the average values, and the errors were estimated by taking into account the spread of our experimental results. The choice of the lower temperature was governed by considerations of convenience, and by the melting point of the hydrocarbon in question.

IV. DISCUSSION

A. The Raman Spectra

In contrast to the n-butane case, it is not feasible to attempt complete frequency assignments for these larger hydrocarbons. However, it is still possible to pick out the Raman lines caused by the most stable rotational isomer, as these will increase in relative intensity on going to lower temperatures, and have hence been marked + in Table I. All the lines observed in the spectra of the solids belong to this class. It would only be possible to further assign the lines resulting from less stable molecular isomers (−) to particular non-stable configurations, if measurements of the energy difference were made in each case. This is not experimentally feasible except for the strong lines in the region 750–900 cm⁻¹, and our measurements on these are discussed in Section IV B.

The most notable feature of the solid spectra shown in Fig. 4 is the enormous simplification obtained when compared with the corresponding spectra of the liquids. This is probably due to the persistence of a single rotational isomer in the solid state in each case, and this is presumably the lowest energy, planar, zig-zag form,[4] as previ-

TABLE II. The energy difference between rotational isomers in n-butane, n-pentane, and n-hexane.

Compound	n-butane		n-pentane		n-hexane	
Line pair(s), cm⁻¹	835–789		862–837		896–867	896–825
Temperature, °K	155	310	154	310	186	310
Intensity ratio (average value)	12.5	3.63	0.69	1.44	2.45 1.39	2.53 1.53
Energy difference cal. mole⁻¹, $-\Delta H$	760±100		450±60		520±70	470±60

ously indicated by x-ray crystal analysis.[9] In the case of n-butane our previous spectroscopic evidence also points to this configuration.[1]

There are marked similarities between the spectra of all these hydrocarbons, and this has been indicated in Fig. 4, by dotted lines connecting related frequencies in the various compounds. From our previous detailed analysis of the n-butane spectrum it can be seen that the frequencies near 1450, 1300, and 1140 cm^{-1} are of the hydrogen deformation type corresponding, respectively, to CH_2 bending, CH_2 wagging, and in-plane CH_3 wagging modes. It further seems reasonable to assign the two series of frequencies near 1050 cm^{-1} and between 900 and 830 cm^{-1} to skeletal stretching modes of the chain. This is substantiated both by the n-butane assignment for the first members of these series, and by the fact that it is in just these regions of the spectra that the greatest numbers of lines disappear on solidification. It is reasonable to suppose that, in general, such skeletal modes would be more sensitive to changes in configuration than the hydrogenic modes, and would hence show up separately in the spectra at room temperature. It is interesting to note from Figs. 1–3 that the positions of the lines corresponding to the lowest skeletal stretching modes of the non-planar configurations in the region 900–750 cm^{-1} are all at lower frequencies than the planar ones. This will have to be taken into account in any complete theoretical treatment of these frequencies. The observed skeletal frequencies are assumed to be the upper and lower limiting frequencies of the stretching vibrations of each molecule. This is certainly true of n-butane, for which a detailed assignment has been made previously,[1] and is suggested for the other hydrocarbons by the dotted correlation lines of Fig. 4. Kohlrausch (see reference 6, p. 206) has also given the expected polarization data and selection rules for the skeletal modes of these hydrocarbons, and showed that the limiting upper and lower frequencies should all be Raman active in agreement with our assumption.

As in this manner we have obtained convincing experimental evidence for the assignment of some

of the skeletal stretching modes of the planar zigzag form, it was of interest to compare these results with previous calculations. A considerable number of calculations have been made, but their correlation with experimental frequencies has previously been somewhat arbitrary because of the presence in the Raman spectra of a multitude of lines caused by other rotational isomers. Such calculations can be divided into two main types, those in which the skeletal modes have been computed on the assumption that no angle changes are involved during the vibrations,[10–13] and more complete treatments in which angle changes are also considered.[3, 14–17]

The results of the most recent calculations made by these methods are shown schematically in Fig. 5 together with the observed limiting skeletal frequencies. This figure includes the results on all the normal paraffins up to C_8. The observed frequencies given for n-octane have been obtained from the liquid spectrum given by Kohlrausch[6] on the assumption that they are close to 1060 and 900 cm^{-1}, as is true for n-hexane and n-heptane.
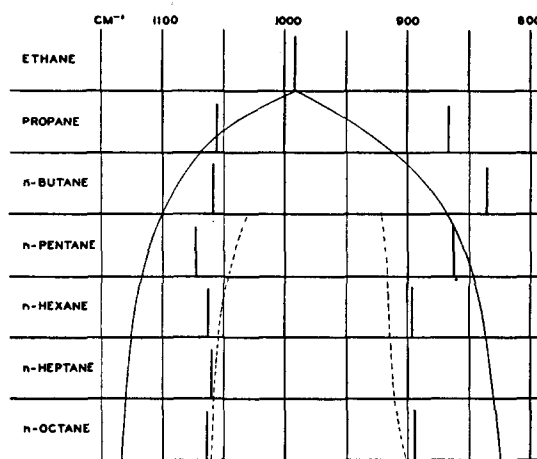
The observed frequencies for each compound

FIG. 5. Calculated and observed limiting skeletal stretching frequencies of the normal paraffins.

[9] See, for example, R. C. Evans, *Crystal Chemistry* (Cambridge University Press, Teddington, England, 1939), p. 326.

[10] E. Bartholomé and E. Teller, Zeits. f. physik. Chemie B19, 366 (1932).
[11] R. Mecke, Zeits. f. physik. Chemie B36, 347 (1934).
[12] B. I. Stepanov, J. Phys. Chem. (U.S.S.R.) 14, 474 (1940).
[13] L. Kellner, Trans. Faraday Soc. 41, 217 (1945).
[14] L. Kassel, J. Chem. Phys. 3, 326 (1935).
[15] J. G. Kirkwood, J. Chem. Phys. 7, 506 (1939).
[16] S. E. Whitcomb, H. H. Nielsen, and L. H. Thomas, J. Chem. Phys. 8, 143 (1940).
[17] C. O. Ahonen, J. Chem. Phys. 14, 625 (1946).

are indicated by the individual heavy lines. The calculated upper and lower limiting frequencies by the first method (assumption of no angle change) are given by the positions in which the continuous curve cuts the appropriate ordinates, and those by the second method (including angle changes) are likewise indicated by the dashed curve. The smooth curve has been drawn directly from the data given by Stepanov,[12] and the dashed curve from Ahonen's[17] calculations on n-butane, n-hexane, and n-octane, modified as described below.

In comparing the experimental frequencies with those calculated by Stepanov, it should be noticed that both tend to constant values with increasing chain length, but that the calculated separation (ca. 300 cm^{-1}) is much larger than the experimental separation (ca. 170 cm^{-1}). It is a general feature of the more detailed treatments that the calculated upper and lower limiting fre-

TABLE III. Statistical weights of rotational isomers in n-paraffins.*

| Compound | Energy above ground state | | | | | |
	0	a	2a	3a	4a	∞
n-butane	1	2	0	0	0	0
n-pentane	1	4	2	0	0	2
n-hexane	1	6(4, 2)	8	2	0	10
n-heptane	1	8(4, 4)	18	12	2	40

* This table is reproduced in part from Pitzer's work (see reference 3).

quencies for the longer chain molecules do not have so great a separation and are hence in better agreement with our experimental value, but calculations that have so far been made do not in any case agree closely with experiment as regards the individual positions of the lines. For example, Ahonen calculates that these frequencies should occur between 1127 and 956 cm^{-1} for n-octane, as compared with the experimental limiting frequencies of 1064 and 894 cm^{-1}. In his calculations Ahonen used force constants derived from the propane molecule, and it is clear that a small change in the stretching constant would give very good agreement between the two sets of data. Accordingly, we have corrected Ahonen's figures in a semi-empirical fashion, assuming that a small change in force constant would give rise to a proportional shift of the frequencies (i.e., neglecting further effects due to angle bending). The factor that we used would correspond, on this assump-

tion, to a change of the stretching force constant from 4.12×10^5 to 3.7×10^5 dynes cm^{-1}. We corrected, in a similar fashion, the frequencies given by him for n-hexane and n-butane, and have used these recomputed values to draw in the dotted curve shown in Fig. 5. It can be seen that in this way good agreement between theory and experiment has been achieved in both the positions and separations between the limiting frequencies in the hydrocarbons n-hexane, n-heptane, and n-octane. It is clear, however, that this treatment fails in the case of n-butane and, by interpolation, for n-pentane. Indeed it is difficult to see how either treatment could account for the peculiar behavior of these frequencies in the lower members of the series. It is probable that these can only be explained in a satisfactory manner by taking into account the fact that rather different bending and stretching constants will apply to the ends as compared to the inner portions of the chain.

B. The Number of Rotational Isomers and the Energy Differences

As mentioned earlier, the improved techniques made possible a determination of the energy difference in n-butane using the line pair at 835–789 cm^{-1}. The result obtained was $-\Delta H = 760 \pm 100$ cal. mole^{-1}, which is to be compared with our previous value of 770 ± 90 cal. mole^{-1}. The exact agreement is perhaps fortuitous, but leaves no doubt as to the general magnitude of the energy difference. This value agrees remarkably well with Pitzer's prediction.[3] According to Pitzer's treatment the general picture for the first four hydrocarbons containing rotational isomers is shown in Table III. In this table are shown the statistical weights of groups of rotational isomers of the same energy, and the molecular compositions of these mixtures can be obtained to a first approximation from the formula

$$g_i \exp(-E_i/RT)/\sum_i g_i \exp(-E_i/RT).$$

In Pitzer's treatment E_i is the appropriate integral multiple of $a = 800$ cal. mole^{-1}, and g_i is the statistical weight given in Table III. Some of the isomers belonging to the same energy level can be further distinguished spectroscopically, because their different spatial configurations will lead to separate frequencies in the spectra. This subdivi-

sion is indicated in Table III for the first levels of n-hexane and n-heptane by the numbers in parentheses. It is easily seen from the molecular models that the maximum statistical weight of any spectroscopically identical species is four. Consequently, we have not carried out this separation for the higher energy isomers on the assumption that the $\exp(-E/RT)$ term will greatly reduce the populations of such states. On the basis of this picture we would predict the following number of strong, polarized Raman lines in the region 900–780 cm^{-1}: n-butane and n-pentane two, n-hexane and n-heptane three. This is based on the very probable assumption that each type of isomer present in quantity will give one such frequency in this region as is the case for the stable, planar, and zig-zag form. The experimental results for n-butane, n-pentane, and n-hexane in this region are shown in Figs. 1–3 and can be seen to be in excellent agreement with these predictions, and provide further evidence for the general correctness of Pitzer's treatment. Although in the case of n-heptane no complete spectrum was obtained at low temperatures, we did investigate the spectral region between 950–800 cm^{-1} on the photoelectric spectrograph. The curves obtained at the high and low temperatures are shown in Fig. 6. In agreement with Kohlrausch,[6] we find three fairly strong frequencies at 899, 846, and 831 cm^{-1}, as predicted above. The weaker shoulder on the side of the 899-cm^{-1} line, which shows up more distinctly in the low temperature run because of the sharpening of the lines, is probably another, non-skeletal, frequency of the stable isomer. The photoelectric measurements on n-butane, n-pentane, and n-hexane were made on sufficiently well resolved lines to yield clear-cut results, the line pair separations given in Table II ranging from 25–46 cm^{-1}, as compared with the 15-cm^{-1} separation of these poorly resolved lines in n-heptane. These measurements lead to the energy differences summarized in Table II. No further discussion of the value obtained for n-butane is necessary. The energy differences obtained for n-pentane and n-hexane are distinctly lower than that for n-butane. In the case of n-pentane we are still dealing, as in n-butane, with rotation about the second C—C linkage, while beginning with n-hexane inner linkages are also contributing different rotational isomers. In the case of
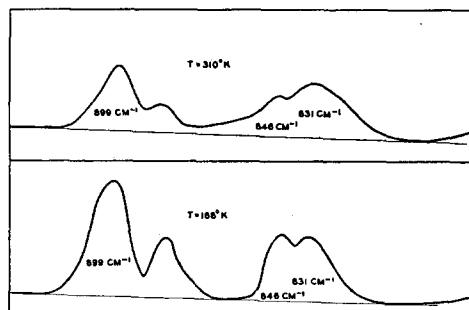

FIG. 6. Photoelectric intensity recording of the Raman spectrum of n-heptane, between 925 and 800 cm^{-1}, at 310°K and at 188°K.

n-hexane there are two spectroscopically different isomers at about the same energy above the ground state. It is not possible to decide unequivocally which of these is the butane analog and which is the new type, but the separation of the line pairs suggests that the 867-cm^{-1} line belongs to the n-butane type isomer, having a corresponding energy difference of 520 cal. mole^{-1}. It was, unfortunately, not possible to derive any quantitative results from our measurements in n-heptane, for, as can be seen from Fig. 6, the overlapping of the lines makes the intensity measurements extremely uncertain. The energy differences in n-pentane and n-hexane are identical within experimental error. As one of the n-hexane values corresponds to rotational isomerism about an internal C—C linkage, it seems likely that this value of about 500 cal. mole^{-1} is the energy difference for all rotational isomers previously considered[3] at 800 cal. mole^{-1} (i.e., those listed in the "a" column of Table III), except of course for the special case of n-butane.

Independent evidence of a less direct type has been cited by Beckett, Pitzer, and Spitzer[18] in support of the original choice of 800 cal. mole^{-1} for the n-butane type energy difference. This was based on the heats of combustion[19] of the liquid dimethyl cyclohexanes and gave a value of 900 cal. mole^{-1}. No experimental evidence concerning the magnitude of these energy differences is so far available in the vapor, and it is possible that our values are not strictly applicable to this phase. On the other hand, it seems probable that in view of the relatively weak intermolecular forces the

[18] C. W. Beckett, K. S. Pitzer, and R. Spitzer, J. Am. Chem. Soc. 69, 2488 (1947).
[19] E. J. Prosen, W. H. Johnson, and F. D. Rossini, J. Research Nat. Bur. Stand. 39, 173 (1947).

TABLE IV. Experimental and calculated gaseous heat capacities of n-pentane and n-hexane.

		n-pentane			n-hexane	
T, °K	Cp exp[a]	Cp° calc. $-\Delta H=$ 500 cal. mole^{-1}	Cp° calc. $-\Delta H=$ 800 cal. mole^{-1}	Cp° exp[b]	Cp° calc. $-\Delta H=$ 500 cal. mole^{-1}	Cp° calc. $-\Delta H=$ 800 ca. mole^{-1}
331	31.3±0.2	31.0	31.5	37.28±0.04	37.1	37.9
427	38.0±0.3	38.6	39.0	45.69±0.05	46.0	46.6

[a] See reference 21.   [b] See reference 23.

energy differences in liquid and vapor hydrocarbons are not very different.

An obvious way to test our results was to compare experimental and calculated thermodynamic properties, using the rounded value of 500 cal. mole^{-1} for the parameter "a" in Pitzer's treatment.[3] In making these calculations, we used the following frequency assignment for the hydrogenic modes of the CH_2 and CH_3 groups (cf. our analysis of the n-butane spectrum[1]): CH_2 group, 2900(2), 1450, 1300, 1250, 750; CH_3 group, 2900(3), 1450(2), 1375, 1140, 950. The upper and lower limiting frequencies of the $C-C$ stretching modes were taken from the solid spectra of the low energy form and from the frequencies of neighboring temperature-dependent Raman lines for the high energy forms. The intermediate stretching frequencies were computed using Stepanov's calculations[12] adjusted so as to fit the experimental values of the extreme frequency interval. The $C-C$ bending modes for n-pentane were taken to be the three observed frequencies for all the isomeric forms, and in the case of n-hexane the four strong observed Raman lines were likewise used. The torsional modes were taken at 120 cm^{-1}. 3300 cal. mole^{-1} was used as the height of the sinusoidal potential barrier hindering the rotation of the terminal methyl groups.

For our purposes the gaseous heat capacity is the most useful thermodynamic property, as it is relatively insensitive to the low lying bending and torsional frequencies which are the least accurate in our assignment. On the other hand, it is sensitive to changes in population between the various energy states, as controlled by the energy difference in which we are interested.

In the case of n-butane our detailed frequency assignment gives almost identical heat capacity contributions with the earlier schematic one of Pitzer,[3] which was subsequently modified[20] to

give better agreement with the experimental results on n-pentane.[21] While Pitzer's later assignment gives somewhat better numerical agreement with the experimental gas heat capacities of n-butane[22] than does our treatment, both calculations are within the experimental errors of the measurements. As they assume the same energy difference between the rotational isomers, the somewhat different results are of no significance from our present point of view.

The experimental gas heat capacities of n-pentane[21] and of n-hexane[23] were compared with calculated values, and the results are summarized in Table IV. No detailed comparisons were made for n-heptane.[24] In the case of both pentane and hexane, using 500 cal. mole^{-1} for the energy difference, the calculated and experimental curves cross between 330° and 430°K (the temperature range of Pitzer's experimental values for n-pentane). In both cases our slope is too high, i.e., the calculated heat capacity increases too rapidly with temperature. This slope could be decreased somewhat by adopting the value of 800 cal. mole^{-1} for the energy difference, but this would raise the calculated curve above the experimental one throughout the entire temperature range. In order to bring these curves into good agreement some modification of Pitzer's treatment appears necessary. In view of the important part played by the higher energy rotational isomers it seems probable that the appropriate energy differences are not represented with sufficient accuracy by simple multiples of the parameter "a." This seems physically reasonable for isomers derived from the planar zig-zag form by successive rotations about neighboring linkages.

ACKNOWLEDGMENTS

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