[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY]

The Molecular Structures of *n*-Pentane, *n*-Hexane and *n*-Heptane[1]

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The molecular structures of gaseous *n*-pentane, *n*-hexane and *n*-heptane have been investigated by the sector-microphotometer method of electron diffraction. The bond lengths for the molecules, in the above order, were found to be, in terms of center of gravity parameters r_g: C–H = 1.118 ± 0.004 Å., 1.118 ± 0.006 Å., 1.121 ± 0.007 Å.; C–C = 1.531 ± 0.002 Å., 1.533 ± 0.003 Å., 1.534 ± 0.003 Å. Angles calculated from r_g internuclear distances were: <C–C–C = 112.9 ± 0.2°, 111.9 ± 0.4°, 112.6 ± 0.3°; <C–C–H = 110.4 ± 0.3°, 109.5 ± 0.5°, 109.8 ± 0.5°. Root-mean-square amplitudes of vibration were: C–H = 0.083 ± 0.004 Å., 0.080 ± 0.005 Å., 0.078 ± 0.007 Å.; C–C = 0.0575 ± 0.003 Å., 0.0575 ± 0.003 Å., 0.051 ± 0.003 Å.; C···H = 0.116 ± 0.005 Å., 0.123 ± 0.005 Å., 0.104 ± 0.005 Å.; C···C = 0.080 ± 0.004 A., 0.080 ± 0.004 Å., 0.076 ± 0.004 Å. The non-systematic standard errors estimated from least squares and other information were found to agree very closely with the root-mean-square deviations between corresponding parameters for the above three molecules and *n*-butane, which was investigated recently, in a comparison including 40 independent parameters. The observed flexibility of the hydrocarbon chains was compatible with that implied by internal rotational barriers deduced by Pitzer from heat capacity data.

Hydrocarbon molecules hold a position of prime importance in chemistry both from their technological significance and from the monumental amount of experimental and theoretical research in which they serve as basic units for comparison. Nevertheless, reliable structural information for even the simplest of these molecules is scant. In addition to precise bond angles and distances, an imperfectly resolved structural problem is the intrinsic flexibility of hydrocarbon chains. Previous investigations of gaseous hydrocarbon molecules by a variety of indirect methods have led to contradictory interpretations. Probably the most reliable approach applied to date is the description in terms of a distribution between rotational isomers as deduced from potential barriers estimated by Pitzer[2] from heat capacity data. A different picture has been offered by Ubbelohde, *et al.*,[3] who have interpreted vapor phase viscosity measurements, molar volumes and entropies of vaporization as indicating that gaseous hydrocarbon molecules are more highly crumpled or coiled than implied by the above statistical description. On the other hand, Stein[4] has suggested from analysis of light scattering depolarization experiments that *n*-hydrocarbon molecules may be more rigidly extended than indicated by the statistical thermodynamic approach. Since electron diffraction provides the most direct geometrical information about free molecular structures that can be derived, it seemed an appropriate approach to aid in the resolution of the problem.

Experimental Procedure

The compounds used in this research were all of synthetic origin and are presumed to be over 99.5% pure. *n*-Pentane was obtained from the Phillips Petroleum Company, *n*-hexane was donated by Professor F. E. Bartell and *n*-heptane was donated by Professor R. S. Hansen. Electron diffraction patterns of the vapors were taken with an r^3 sector, using the University of Michigan apparatus.[5] Specimen pressures of 160, 150 and 50 mm. were used for the *n*-pentane, *n*-hexane, *n*-heptane, respectively. The temperature of the specimen bulb was 305°K. The diffraction data were processed in the same way as the data for *n*-butane, as described earlier.[6]

Indices of resolution, $R = M_{\text{expt}}/M_{\text{theor}}$, were 0.89 to 0.99 for the 10 cm. camera data and 0.75 to 0.90 for the 25 cm. data. The failure of R to be unity was due principally to a uniform delocalization of the specimen in the diffraction chamber, and corrections for this effect[7] were made for all structural parameters.

Structure Analysis

A procedure described fully elsewhere[8] was used for processing and analyzing data with the IBM 650 digital computer. Parameters were obtained by least squares procedures, and corrections were included for non-nuclear scattering, asymmetry of vibrations (in the locating of the center of gravity distances between bonded pairs of atoms) and Fourier integral termination errors. Corrections for the failure of the Born approximation were applied to the amplitudes of vibration of the C–H pairs using the phase shifts of Hoerni and Ibers.[9] The formula suggested by Bartell, Brockway and Schwendeman[10] for this purpose gives, in general, insufficient correction. In the computation of the experimental radial distribution functions, $f(r)$, the value of b used in the damping function was 0.00211.

In the calculation of structural models and in the initial analysis of radial distribution curves, it was assumed that the structures could be described in terms of a distribution between the rotational isomers listed in Table I. It was further assumed, for a given molecule, that C–C and C–H bonds and C–C–C and C–C–H angles had the same value wherever they occurred in the molecule, whatever the angle of rotation about the C–C bonds.

Theoretical reduced intensity values were used in the integrand of $f(r)$ in the non-definitive experimental region inside $q \sim 12$ and in the correction of experimental data for non-nuclear scattering. The theoretical models used included all internuclear distances and all probable internal rotational configurations for the molecules *n*-pentane and *n*-hexane. For *n*-heptane all internuclear distances

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[1] This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[2] K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940); *Ind. Eng. Chem.*, **36**, 829 (1944).

[3] J. C. McCoubrey, J. N. McCrea and A. R. Ubbelohde, *J. Chem. Soc.*, 439, 1961 (1951).

[4] R. S. Stein, *J. Chem. Phys.*, **21**, 1193 (1953).

[5] L. O. Brockway and L. S. Bartell, *Rev. Sci. Instr.*, **25**, 569 (1954).

[6] R. A. Bonham and L. S. Bartell, THIS JOURNAL, **81**, 3491 (1959).

[7] L. S. Bartell, *J. Appl. Phys.*, in press.

[8] R. A. Bonham and L. S. Bartell, to be published.

[9] J. A. Ibers and J. A. Hoerni, *Acta Cryst.*, **7**, 405 (1954).

[10] L. S. Bartell, L. O. Brockway and R. H. Schwendeman, *J. Chem. Phys.*, **23**, 1854 (1955).

TABLE I

ROTATIONAL ISOMERS ASSUMED IN COMPUTATIONS

Configuration	Multiplicity[a]	% Present[b]
n-Pentane		
TT	1	42.6
TG	4	50.1
GG	2	7.3
n-Hexane		
TTT	1	29.0
TTG	4	34.0
TGT	2	17.0
TGG	4	10.0
GTG	4	10.0
GGG	2	(0)
n-Heptane		
TTTT	1	19.3
TTTG	4	22.2
TTGT	4	22.2
TTGG $\simeq$ TTG + TGG − TG	4	6.8
GTTG $\simeq$ 2TTG − TT	4	6.8
TGTG $\simeq$ TGT + GTG − TG	8	13.6
TGGT $\simeq$ 2TGG − GG	2	3.4
TGGG $\simeq$ TGG + GGG − GG	2	1.9
GTGG $\simeq$ GTG + TGG − TG	8	3.8
GGGG	2	(0)

[a] Takes into account both G and G′ conformations. Configurations with G and G′ adjacent are considered to be sterically unreasonable and are given zero weight.
[b] Based on assumed difference in energy between *trans* and *gauche* conformations of about 700 cal./mole. Experimental parameters of Table II are insensitive to the value assumed.

for rotational models accounting for 60% of the molecules in the specimen were included in computations of intensity functions. For the remaining 40% the approximations indicated in Table I were used to reduce to practicability the handling of the enormous number of relatively unimportant internuclear distances involved. These approximations, which utilized linear combinations of models of *n*-hexane and *n*-pentane, guaranteed exact treatments of all radial distribution peaks from which the reported distances and angles in Table II were derived. The areas of features in $f(r)$ at large r are probably somewhat low, but the shape of the curve is approximately correct. Even with the above approximations the number of distances included in the calculations is several hundred. Reliable numerical derivation and handling of this large number of parameters was feasible only with the application of a program of electronic computation.

Experimental radial distribution functions for the molecules are shown in Figs. 1–3. Internuclear CC and CH distances for the three most important rotational configurations for each molecule are indicated. The lengths of the lines drawn for a given configuration, if divided by r, would be proportional to the scattering powers as portrayed by $f(r)$. The distances, angles and amplitudes reported in Table II were derived from the experimental $f(r)$ curves by weighted least squares fits with theoretical curves from 0.9 to 1.725 Å. (range I) and 2.0 to 2.9 Å. (range II), taking careful account of all interfering peaks. The amplitudes of vibration reported correspond to the root-mean-square amplitudes of the gaussian peaks best fitting the experimental peaks. Uncertainties quoted for amplitudes do not reflect possible effects of asymmetry of vibration on the actual mean-square amplitudes. These effects are probably not larger than the stated uncertainties.

TABLE II

STRUCTURAL PARAMETERS DERIVED FROM RADIAL DISTRIBUTION CURVES AND ASSIGNED STANDARD ERRORS

	n-Butane	*n*-Pentane	*n*-Hexane	*n*-Heptane	Av.	Std. dev.	Calcd. value
r_g, Å.							
C–H	1.108 ± 0.004	1.118 ± 0.004	1.118 ± 0.006	1.121 ± 0.007	1.116_3	0.0051	....
C–C	1.533 ± $.002_5$	1.531 ± .002	1.533 ± .003	1.534 ± .003	1.532_8	.0010	....
C–H	2.183 ± .005	2.188 ± .004	2.178 ± .005	2.185 ± .004	2.183_5	.0036	....
C–C	2.547 ± .005	2.552 ± .003	2.541 ± .004	2.553 ± .003	2.548_2	.0045	....
<C–C–C	112.4 ± .3°	112.9 ± .2°	111.9 ± .4°	112.6 ± .3°	112.4_5°	.36°	....
<C–C–H	110.5 ± .5°	110.4 ± .3°	109.5 ± .5°	109.8 ± .5°	110.0_5°	.42°	....
l, Å.							
C–H	0.078 ± 0.004_5	0.083 ± 0.004	0.080 ± 0.005	0.078 ± 0.007	0.079_9	.0021	0.078[a]
C–C	$.055_5$ ± .003	$.057_5$ ± $.002_5$	$.057_5$ ± $.002_5$	.051 ± .003	$.055_3$	.0029	.050[a]
C–H	.106 ± .006	.116 ± .005	.123 ± .005	.104 ± .005	.112	.0077	.11[a]
C–C	.079 ± .005	.080 ± $.003_5$	.080 ± $.003_5$	.076 ± $.003_5$	$.078_8$	.0016	.069–0.079
$\sigma(\mathrm{rf})_{\mathrm{I,II}}$	.055, 0.060	.044, 0.044	.066, 0.042	.120, 0.054	......	....	....
$R_{\mathrm{I,II}}$	.878, 0.871	.897, 0.898	.891, 0.880	.985, 0.987	......	....	....

[a] Calculated by Kuchitsu for *n*-butane from force constant data, reference 12. The ambiguity for C–C results from an uncertainty in spectroscopic assignments.

Angles were calculated from center of gravity parameters, r_g, and the uncertainties quoted refer only to the uncertainty of the r_g parameters. The interpretation of such angular parameters in terms of, say, mean angles, is at present uncertain by an amount probably as great as the experimental uncertainties, owing to the large amplitudes of bending. This interpretational uncertainty, however, is no greater than that in spectroscopic analyses of angular parameters for similar molecules.

The analysis of the distribution between rotational isomers is, as yet, incomplete. The effect of varying the ratio of isomers in the assumed structural models upon the radial distribution curves is illustrated for *n*-pentane and *n*-hexane in Figs. 1 and 2. Curves B and C assume 100% *trans*, and 100% *gauche*, respectively, in the models used in the inaccessible region of scattering angle. The heavy lines in Figs. 1–3 are based on the models of Table I.

The standard errors listed in Table II were com-

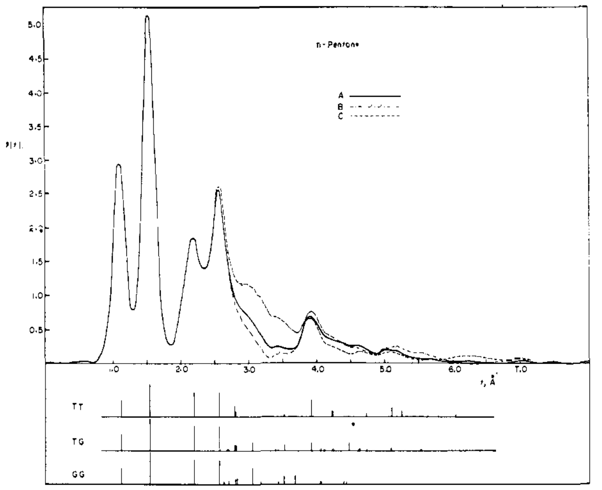

Fig. 1.—Experimental radial distribution function for *n*-pentane. Assumed in intensity computed for inaccessible low angle range: (A) model of Table I; (B) 100% *trans;* (C) 100% *gauche.*

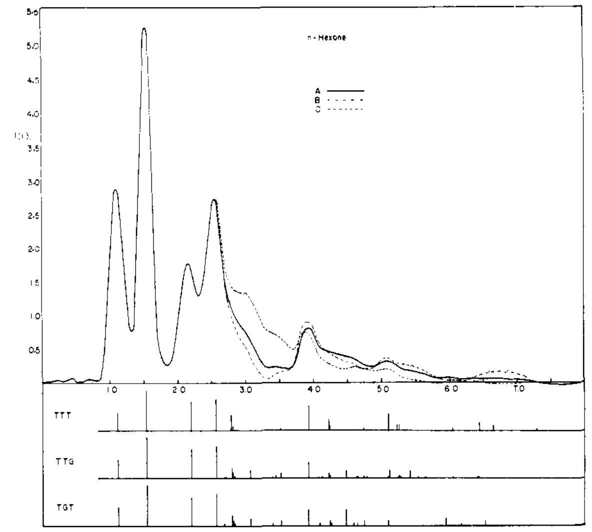

Fig. 2.—Experimental radial distribution function for *n*-hexane. Assumed in intensity computed for inaccessible low angle range: (A) Model of Table I; (B) 100% *trans;* (C) 100% *gauche.*

puted as described elsewhere.[6,8] The effect of random intensity errors was estimated for each molecule separately, from the least squares fitting of the $f(r)$ functions. The standard scale factor error, including the errors in the camera distance and chart scale of the microphotometer records, was taken to be 1.2 parts per thousand. The magnitude and direction of this error is not identical for all molecules, since the largest part of the error is the camera distance which was unstable by, perhaps, 1 part per thousand. The other main error results from the uncertainty in the index of resolution and its failure to be unity. The effect upon the internuclear distances was arbitrarily taken to be half of the correction due to the gas spread. The associated error in amplitudes of vibration was taken, perhaps too severely, to be 0.7 $\delta R/R \simeq 4\%$. The magnitudes of the various errors in the present investigation are similar to those for *n*-butane, for which molecule they are recorded in more detail.[6] The over-all errors contain all known sources of error except those associated with the imperfectly understood approximations in electron scattering theory and the interpretational errors mentioned above.

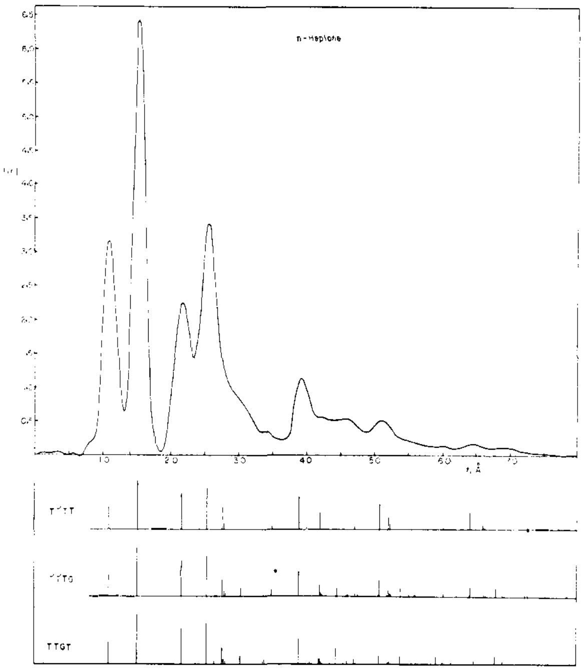

Fig. 3.—Experimental radial distribution function for *n*-heptane.

Results

The experimental reduced intensity curves plotted in Fig. 4 illustrate the sharpening of the diffraction features accompanying the addition of longer intramolecular distances as the molecular size increases from *n*-butane to *n*-heptane. These curves may be compared with the corresponding theoretical curves in Fig. 5, calculated for models derived from the radial distribution curves. The development of longer distances is evident in the experimental radial distribution curves for the same molecules illustrated in Fig. 6. Within the limits of validity of the assumptions stated above about

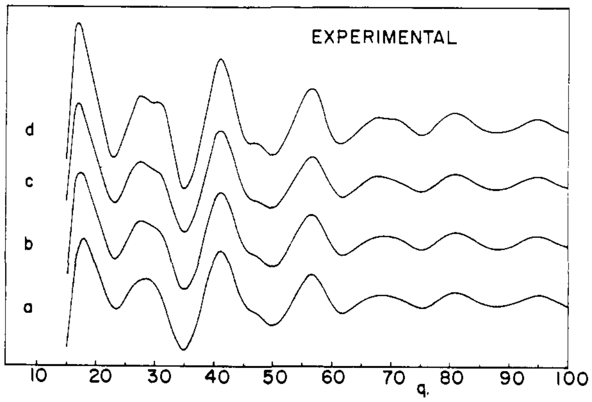

Fig. 4.—Experimental reduced intensity curves for: (a) *n*-butane; (b) *n*-pentane; (c) *n*-hexane; (d) *n*-heptane.

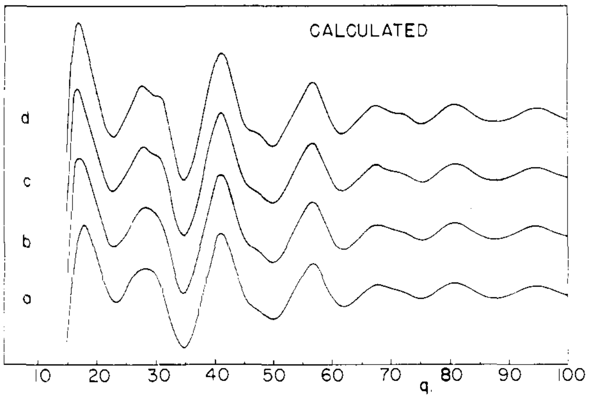

Fig. 5.—Theoretical reduced intensity curves for: (a) *n*-butane; (b) *n*-pentane; (c) *n*-hexane; (d) *n*-heptane.

molecular structure, the first four peaks of each distribution curve determine all structural parameters except the mean angles of twist of the rotational isomers about C–C bonds and the population distributions. The experimental results derived from these peaks are tabulated for the molecules of the present investigation and also for *n*-butane[6] in Table II.

Noteworthy is the relatively high apparent accuracy of the structural parameters. The reporting of such accuracy in electron diffraction work is justified only if the corrections discussed above have been carefully made and if the operational definition of parameters has been explicitly specified. It may be noted that center of gravity distances, r_g, are often 0.01 Å. or more greater than equilibrium distances, r_e.[11] In addition to the structural parameters, two parameters characterizing the quality of the radial distribution curves are reported in Table II. The standard deviations

$$\sigma(rf) = \{\Sigma r^2_k[f_e(r_k) - f_0(r_k)]^2/N\}^{1/2}$$

based on observed and calculated radial distribution curves and the apparent indices of resolution, *R*, are reported for the ranges I and II which were fitted. Ranges I and II were from 0.9 to 1.725 Å., and 2 to 2.9 Å., respectively, except for *n*-heptane where range I was slightly wider. In the weighting of the least-squares curve fittings it was assumed that the errors tend to damp according to r^{-1}. The relative constancy of $\sigma(rf)$ lends support to this assumption. The standard deviations, $\sigma(f)$, of the $f(r)$ curves themselves may be found approximately by dividing $\sigma(rf)$ by r. The root-mean-square deviations average less than 1% of the maximum values of the $f(r)$ curves. A different measure of the correctness of the relative areas of peaks is indicated by a comparison of the *R* values obtained for ranges I and II.

The present data provide the first experimental check of the method of calculation of standard errors developed elsewhere.[8] While there is no reason to believe that the corresponding parameters in the present molecules should be identical, the scatter of the independent results should give a reasonable estimate of non-systematic errors.

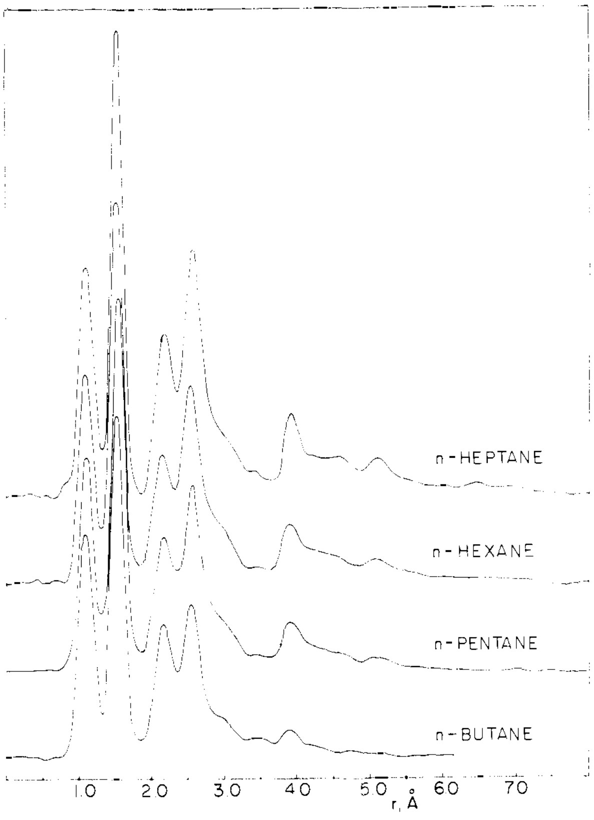

Fig. 6.—Comparison of experimental radial distribution functions.

It is reassuring to note that the standard deviations observed for forty independent r_{ij} and l_{ij} values (ten groups of four of which two groups are not listed in Table II) are within 10%, on the (geometric) average, of the purely random contributions to the standard errors calculated as discussed above.

The experimental root-mean-square amplitudes of vibration are in excellent agreement with approximate values calculated for *n*-butane by Kuchitsu[12] from spectroscopic data. Only for the C–C bond is there an apparent discrepancy and that cannot be regarded as serious.

The constancy of the C–C bond length in the series is striking. The trend of the C–H bond to increase as the number of carbon atoms increases suggests, though not compellingly, that methylene C–H bonds are longer than methyl CH bonds. This conclusion is also implied by the force constants assigned by Simanouti,[13] in which C–H force constants for methylene groups are lower than for methyl groups. The C–C–C angle is clearly greater than the tetrahedral angle, a fact that has often been observed before.

The experimental distances and angles are in approximate agreement with the corresponding parameters observed in other studies of paraffin hydrocarbons as shown in Table III. The electron diffraction values for ethane have been increased by l^2_{ij}/r_{ij} to make them correspond more

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(11) L. S. Bartell, *J. Chem. Phys.*, **23**, 1219 (1955). The symbol r_g denotes $\int_0^\infty rP(r)\,dr$, and has been referred to as $r_g(0)$ in previous papers by Bartell.

(12) K. Kuchitsu, *Bull. Chem. Soc. Japan* (in press).

(13) T. Simanouti, *J. Chem. Phys.*, **17**, 848 (1949).

TABLE III

OTHER STUDIES OF PARAFFIN HYDROCARBONS

Substance	Method	C–H	C–C	C–C	<C–C–H	<C–C–C
Ethane[a]	E.D.	1.113[b]	1.538[b]	....	109.5°	....
Ethane[c]	E.D.	1.120 ± 0.03[b]	1.538 ± 0.016[b]	....	110.5 ± 3.5°	....
Ethane[d]	I.R.	1.102	1.543	....	109.6°	....
n-Propane[e]	M.W.	(1.090)	1.537	2.543	....	111.7°
Isobutane[f]	M.W.	(1.090)	1.534	....	(110.4°)	(111.2°)[g]
n-Butane[h]	E.D.	1.099 ± 0.003	1.540 ± 0.003	2.554 ± 0.005	110.5 ± 0.25°	112.1 ± 0.15°
n-$C_{36}H_{74}$[i]	X.R.	....	1.534 ± 0.006	2.546 ± 0.004	....	112.2 ± 0.3°
n-$C_{23}H_{48}$[j]	X.R.	....	....	2.549 ± 0.004	....	....
Diamond[k]	X.R.	....	1.5445	....	....	109.47°

[a] A. Almenningen and O. Bastiansen, *Acta Chem. Scand.*, 9, 815 (1955).
[b] Values increased by l_{ij}^2/r_{ij} to correspond more nearly to r_g parameters.
[c] K. Hedberg and V. Schomaker, THIS JOURNAL, **73**, 1482 (1951).
[d] G. E. Hansen and D. M. Dennison, *J. Chem. Phys.*, **20**, 316 (1952).
[e] D. R. Lide, 134th Meeting of American Chemical Society, Chicago, September 1958, paper 28, Petroleum Chemistry.
[f] D. R. Lide and D. E. Mann, *J. Chem. Phys.*, **29**, 914 (1958).
[g] Estimated for present purposes by comparison of *n*-butane and neopentane.
[h] K. Kuchitsu, reference 12.
[i] H. M. M. Shearer and V. Vand, reference 15.
[j] A. E. Smith, reference 16.
[k] K. L. Lonsdale, *Phil. Trans. Roy. Soc.*, **A420**, 1219 (1947).

nearly to center of gravity parameters, r_g. The spectroscopic parameters for ethane, *n*-propane and isobutane correspond to neither center of gravity nor equilibrium values due to effects of zero point vibrations but agree reasonably well with the values obtained in the present investigation. The very recent electron diffraction results of Kuchitsu for *n*-butane[12] agree remarkably well with the results for *n*-butane obtained in the first paper of this series in bond angles, angles of twist about C–C bonds and distribution between *trans* and *gauche* conformations. The agreement between bond distances is not quite as good, but the discrepancies are not significant, according to Cruickshank's[14] criterion. The X-ray results of Shearer and Vand[15] and of Smith[16] for the crystalline long-chain hydrocarbons are in excellent agreement with the present results.

The discrepancy between the C–C bond length in diamond, long regarded as the standard C–C length, and the bond length in the present *n*-hydrocarbons, appears to be real. It has tentatively been explained elsewhere[17] as due to the greater magnitude of *gauche* interatomic van der Waals repulsions in the diamond.

The distribution between rotational isomers has not yet been analyzed exhaustively as it was in the case of *n*-butane, owing to the greatly increased complexity of calculations in the present case. It is clear from the well-developed distances appearing at 4 Å. and beyond, however, that the molecules cannot be as indiscriminantly crumpled and coiled as implied by Ubbelohde, *et al.*[3] On the other hand, the C–C peaks corresponding to all *trans* configurations are too low to indicate the presence of more than a small fraction of rigidly extended molecules. The data appear to be compatible with internal rotational barriers deduced by Pitzer from heat capacity data. A more nearly complete analysis of the diffraction data in terms of the flexibility of the hydrocarbon chains will be reported later.

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(14) D. W. J. Cruickshank and A. P. Robertson, *Acta Cryst.*, **6**, 698 (1953).

(15) H. M. M. Shearer and V. Vand, *ibid.*, **9**, 379 (1956).

(16) A. E. Smith, *J. Chem. Phys.*, **21**, 2229 (1953).

(17) L. S. Bartell, THIS JOURNAL, **81**, 3497 (1959).