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

The Molecular Structure and Rotational Isomerization of *n*-Butane[1,2]

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The structure of gaseous *n*-butane was investigated by the sector-microphotometer method of electron diffraction. The major internuclear distances, $r_g(0)$, were found to be C–H = 1.108 ± 0.004 Å., C–C = 1.533 ± 0.003 Å. and C---C = 2.547 ± 0.005 Å., and angles were ∠C–C–C = 112.4 ± 0.3° and ∠C–C–H = 110.5 ± 0.5°. It was determined that *gauche* and *trans* rotational isomers were present, with a *trans* concentration of 60 ± 15% at about 14°C. The mean azimuthal angle of the *gauche* form was 63 ± 8° and the *trans* form appeared to be twisted from a planar configuration by a root-mean-square angle of approximately 13°. The rotational barriers implied by the diffraction results are compatible with those deduced for gaseous *n*-butane by Pitzer from heat capacity data. Amplitudes of vibrations were determined and found to agree well with amplitudes calculated by Morino, *et al.*, from force constants.

It is remarkable now when such a great body of accurate structural information exists for relatively complicated molecules that there are scarcely any definitive results for many of the simplest molecules of all, the normal hydrocarbons. The last electron diffraction studies of members higher than ethane were made about twenty years ago when the accuracy of the method was severely limited. Spectroscopic investigations are difficult because of the small dipole moments but determinations for a few members promise to be forthcoming soon.

There is no unanimity at present about the precise value of the normal (C–C) carbon–carbon single bond distance, one of the most basic distances in theories of valence. With this in mind, and also as part of a larger program to establish the degree of flexibility of *n*-hydrocarbon chains, an investigation of the molecular structure of *n*-butane was undertaken. *n*-Butane is the simplest hydrocarbon capable of exhibiting *trans–gauche* rotational isomerization, and a modern sector-microphotometer electron diffraction study offered the possibility of a direct structural determination to complement indirect inferences drawn by Pitzer[3] from heat capacity studies.

Experimental Procedure

A sample of *n*-butane of purity greater than 99.5% was used as obtained from the Matheson Company. Electron diffraction patterns were taken with the University of Michigan rotating sector apparatus[4] and recorded on Kodak Medium Lantern Slides using 40 kv. electrons with an r^3 sector. Experimental procedures followed those previously described.[4] A total of 18 diffraction plates were taken at 25 cm. and 10 cm. camera distances of which 4 apparently flawless plates covering each of the ranges $8 \leqslant q \leqslant 42$ and $21 \leqslant q \leqslant 105$ were carefully selected for analysis. The plates were spun rapidly about their centers during microphotometry to average out emulsion irregularities.

Intensities appeared sensitive to molecular scattering features to 0.1% or better. The index of resolution, $R = M_{\text{expt}}/M_{\text{theor}}$, was found to be about 0.88 for the plates covering the moderate to large angle scattering but only 0.78 for the small angle plates. These values are not as favorable as the values (generally about 0.95) obtained in earlier investigations with the same apparatus. It could be concluded from a knowledge of the characteristics of the diffraction chamber and the angular variation of the extraneous scattering responsible for the depression of the index of resolution that the extraneous scattering arose from a nearly uniform distribution of gas sample in the chamber. Quantitative calculations of the effect of the specimen delocalization upon the measured internuclear distances and amplitudes of vibrations were made and showed that shifts of the order of 10^{-3} Å. are involved for distances but not for amplitudes. The parameters reported below have been corrected for this small effect.

Structure Analysis

A procedure to be described fully elsewhere was used for processing and analyzing data with the IBM 650 digital computer. It resembled the pro-

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[2] Presented in part at the 1958 meeting of the American Crystallographic Association, Milwaukee, Wisconsin, June 26, 1958.

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

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

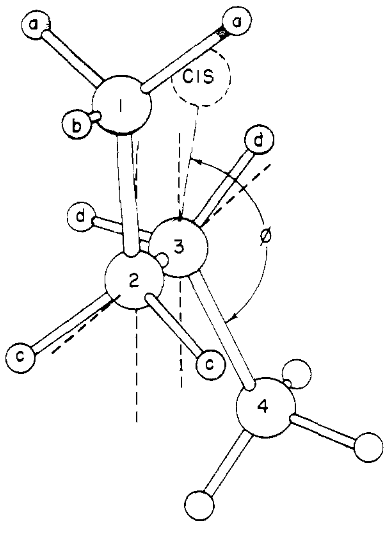

Fig. 1.—Structure of *n*-butane: the azimuthal angle ϕ is approximately ±60° for the *gauche* isomer and approximately 180° for the *trans* isomer.

cedure of Bartell, Brockway and Schwendeman[5] but replaced manual handling of data wherever practicable by high speed digital computation, computed quantities more rigorously and obtained structural parameters more objectively by least squares methods. Included were corrections for non-nuclear scattering, asymmetry of vibrations of bonded pairs of atoms and Fourier integral termination errors.

The radial distribution function, $f(r)$, was computed using a summation ($\Delta q = 1$) closely approximating the expression

$$f(r) = (\pi^2/100) \int_0^{q_{\max}} q\, M_c\,(q)[\exp(-\pi^2 b q^2/100)]\, \sin\,(\pi q r/10)\, dq$$

where the $M_c(q)$ values for each range of q were adjusted to an index of resolution of 0.88, the value for the dominant range. The value of b used was 0.00211. Theoretical $M_c(q)$ values grafted onto the inaccessible region at very small scattering angles for use in the integrand of $f(r)$ included all internuclear distances that occurred in the molecule, even hydrogen–hydrogen distances. In the subsequent resolution of the radial distribution curve, all distances were taken into account.

Reduced theoretical molecular intensity curves were calculated according to the expression

$$M(q) = 10R \sum_i \sum_j{}' c_{ij}\, \mu_{ij}\, [\exp\,(-\pi^2 l^2{}_{ij} q^2/200)]\,[\sin\,(\pi q r_{ij}/10)]/\pi q\, r_{ij}$$

where $M = [(I_{\text{tot}}/I_{\text{background}})^{-1}]$, l_{ij} is the root-mean-square amplitude of vibration of the atom pair i and j, $[r_{ij} + (l_{ij}{}^2/r_{ij})]$ is the center of gravity, $r_g(0)$, of the probability distribution, $P_{ij}(r)$, and $\mu_{ij}(q)$ is a function expressing the effect of atomic scattering factors.[5] Reduced constant coefficient curves $M_c(q)$ for Fourier analysis were calculated by taking $\mu_{ij} = 1$ in the above equation.

Parameters Independent of Internal Rotation.—There are three carbon–carbon bonds in *n*-butane about which internal rotation can occur. The present diffraction data are not sensitive to the detailed characteristics of rotation about the 1–2 and 3–4 bonds shown in Fig. 1 but suggest that the terminal methyls are in staggered configurations. For the purpose of analysis the methyls were assumed to be staggered and librations of the groups were accounted for by appropriate temperature factors. It was further assumed to make the analysis tractable that (a) the structure can be described in terms of a distribution between *trans* and *gauche* rotational isomers as identified in Fig. 1, (b) the *trans* isomer has C_{2h} symmetry when $\phi = 180°$ and maintains the same basic skeletal parameters when librating about the 2–3 bond, (c) the *gauche* isomer is identical to the *trans* isomer except for the azimuthal angle, ϕ, (d) all C–C and all C–H bonds have the same length,[6] and (e) all C–C–H angles are the same. This assumption turns out to be only trivially different from one invoking 3-fold symmetry of the terminal methyl groups.

The above assumptions reduce the problem to a determination of a small number of parameters, namely, the C–H and C–C bond distances, the C–C–C and C–C–H angles, ϕ for the *trans* and *gauche* isomers, the ratio of *trans* to *gauche* isomers and the amplitudes of vibrations of the atom pairs of interest.

The first four peaks in the experimental radial distribution curve shown in Fig. 2 determine completely (within the validity of the above assumptions) the structural parameters which are independent of the internal rotation. The first two peaks correspond to C–H and C–C bonds and can be resolved and characterized directly without interference from other peaks. The next two, indicating non-bonded C---H and C---C distances, are overlapped by low amplitude and relatively broad H–H peaks and by the foot of a longer non-bonded C---H peak. The positions of the mildly interfering peaks are geometrically related to the positions of the first four strong peaks, however, so that it is possible to establish the desired peaks precisely by a rapidly converging series of successive approximations. The final parameters were determined by a least squares procedure fitting peaks to the curve from which the H–H contribution had been subtracted. A comparison between the experimental and calculated curves from 2 to 4 Å. assuming 55% *trans* isomer is shown in Fig. 3. The calculated curve in Fig. 3 was taken from a least squares computer program output which had converged for the 2.2 and 2.5 Å. components but was slightly short of convergence for the 2.8 and 3.9 Å. components. The root mean square deviation between the experimental and computed $f(r)$ curves is 0.024, a value 0.51% of the maximum value of the main C–C peak.

The least squares values for the above parameters, along with others to be discussed later, are presented in Table I. Also included are experimental root-mean-square amplitudes of vibration.

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

(6) The constancy, to within 0.001 Å. of a mean value, of the C–C bonds of n-C_4H_{10}, n-C_5H_{12}, n-C_6H_{14} and n-C_7H_{16} studied in our laboratory lends support to the reasonableness of this assumption. The C–H bonds were found to vary by less than 0.006 Å. from a mean value in the same compounds.

TABLE I

n-BUTANE PARAMETERS DERIVED BY LEAST SQUARES FROM RADIAL DISTRIBUTION CURVE

∠C–C–C = 112.4 ± 0.3°, ∠C–C–H = 110.5 ± 0.5°, ϕ(*gauche*) = 63 ± 8°, *trans* root-mean-square deviation from planarity = 13 ± 5°, % *trans* = 60 ± 15%

Peak	$r_g(0)$, Å.[a]	$\sigma_r(r)$[b]	$\sigma_{tot}(r)$	$r_g(0)$calcd.[c]	l_{ij}(e.d.), Å.	$\sigma_r(l)$[b]	$\sigma_{tot}(l)$	l_{ij}, calcd.[d]
C–H	1.108	0.0035	0.004	(1.108)	0.0780	0.0031	0.0045	0.078
C–C	1.533	.0014	.0025	(1.533)	.0555	.0014	.003	.050
C--H	2.183	.0046	.005	(2.183)	.106	.0045	.006	.11
C_1--C_3	2.547	.0037	.005	(2.547)	.079	.0032	.005	.079
C_1--H_d C_3--H_a	2.78	.019	....	2.777	.18	.014	.04	...
C_3--H_b	3.50	.05	....	3.507	.13	.05	.05	...
gauche C_1C_4	3.072	.015[e]	....	3.049	.109	.016[e]	.016[e]	...
trans C_1C_4	3.900	.008[e]	....	3.915	.083	.014[e]	.014[e]	...

[a] $r_g(0)$ is the center of gravity of the internuclear probability distribution (see reference 14). [b] Standard error from random intensity errors, not including error in scale factor. [c] Distance computed for rigid framework with ϕ(*gauche*) = ±60°. ϕ(*trans*) = 180°. [d] Reference 11. [e] Includes effect of uncertainty in % *trans*.

Approximate standard errors, $\sigma_r(\theta_i)$, due to random intensity errors but not including the scale factor error of about 1.2 parts per thousand, were estimated using the formula where θ_i represents either

$$\sigma^2_{r(\theta_i)} = \left\{ \sigma^2(f) \int_0^\infty p(r)\,dr \Big/ \int_0^\infty p(r)(\partial f_c(r)/\partial\theta_i)^2 dr \right\} \quad (1)$$

r_{ij} or l_{ij}, and $\sigma^2(f)$ is the mean-square deviation between the experimental and calculated $f(r)$ in the vicinity of the peak of interest. The plausible weighting function $p(r) = (\partial f_c(r)/\partial\theta_i)^2$ was used which results in a computed deviation of approximately 80% that of the maximum possible shift in θ_i capable of being caused by an error of maximum amplitude $\sqrt{2}\ \sigma(f)$, provided the peak is isolated. For severely overlapping peaks the value of $\sigma(\theta_i)$ calculated according to eq. 1 may be several-fold too low.

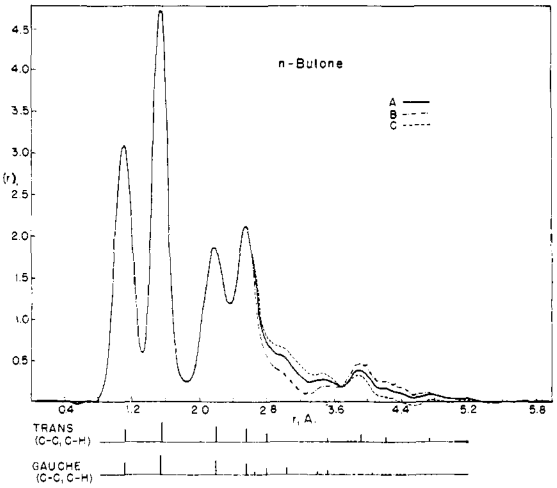

Fig. 2.—Radial distribution curve for *n*-butane—theoretical models used for small angle scattering assume: (A) 55% *trans;* (B) 100% *trans;* (C) 0% *trans.*

After good values of the important skeletal parameters are deduced from the radial distribution curve, it is informative to examine the consequences of small variations in the angular parameters by an intensity correlation procedure. The procedure illustrated in Fig. 4 follows that introduced by Morino, *et al.*,[7] and makes use of "correlation background functions," $I_b(q)$, defined by

$$I_b(q) = I_0(q)/(1 + RM(q)_{\text{theor}})$$

where $I_0(q)$ is the leveled experimental intensity curve, and $M(q)_{\text{theor}}$ is the reduced theoretical intensity curve calculated for an assumed model, including atom form factor effects. Properly, optimum values of the index of resolution, R, and the internuclear distance scale factor must be used for each model, making the method practicable only when fast digital computational facilities are available. At its best, this method is more powerful than the conventional intensity correlation procedure. It is reassuring to note that the model giving the smoothest background function agrees very well with the model deduced by the radial distribution method.

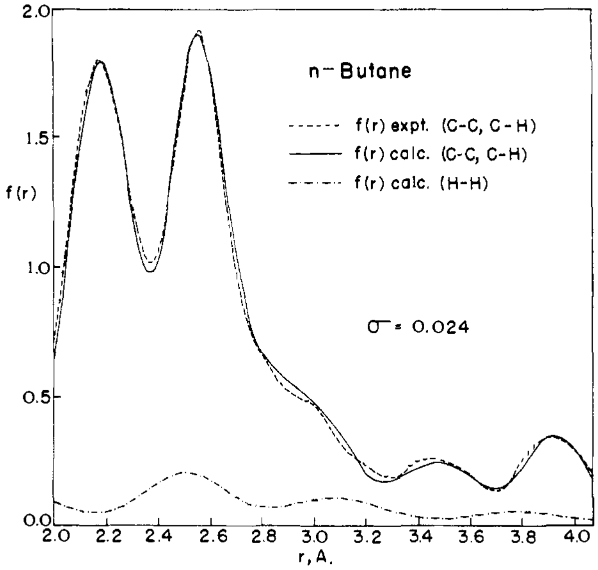

Fig. 3.—Comparison of experimental and calculated radial distribution curves, assuming 55% *trans.*

Internal Rotation.—The problem of determining the ratio of *trans* to *gauche* isomers is more subtle than the above direct analyses. The two isomers begin to differ in their radial distributions of distances beyond about 2.6 Å. If an accurate absolute radial distribution curve were experimentally observable, it would be a simple matter to establish

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[7] Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, **28**, 175 (1958); Y. Morino and E. Hirota, *ibid.*, **28**, 185 (1958).

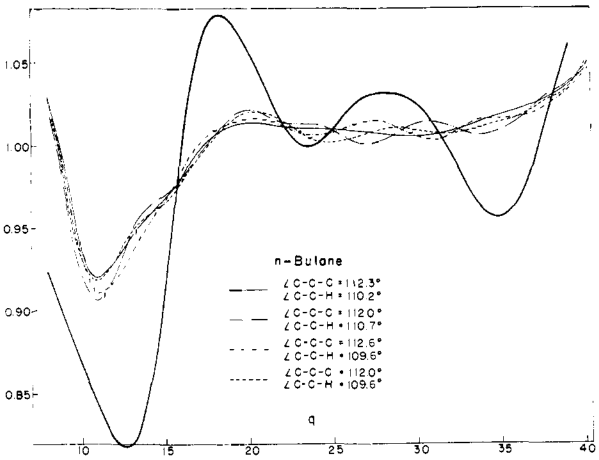

Fig. 4.—Correlation backgrounds, $I_b(q)$, as a function of C–C–C and C–C–H angles; the heavy line represents $I_0(q)$, the experimental intensity.

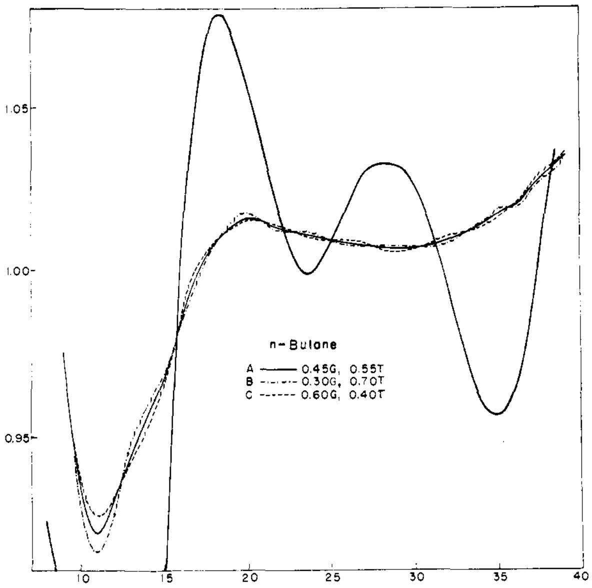

Fig. 5.—Correlation backgrounds, $I_b(q)$, as a function of the *trans* to *gauche* ratio. The heavy line represents $I_0(q)$, the experimental intensity.

the ratio from a direct study of the areas in various ranges of distance. Such a curve is unavailable. The general distribution of area in the experimental distribution curve is dictated by the theoretical model grafted onto the inaccessible small angle scattering range. Nevertheless, the detailed structure of the envelope is determined by experiment. The effect on the experimental radial distribution curve of varying the *trans* to *gauche* ratio is illustrated in Fig. 2. The theoretical models grafted onto the experimental intensity data from q = 0 to q = 13 contain (A) 55% *trans* and (B) 100% *trans* and (C) 0% *trans* concentrations. The humps in all envelopes at 3.0, 3.9, 4.2 and 4.7 Å. suggest appreciable fractions of both isomers.

The most direct simple determination of the ratio can be made by estimating the area concentrated over and above the general background in the C_1---C_4 *trans* peak at 3.9 Å. For each of the curves, (A), (B) and (C), an area was obtained corresponding to roughly 68 ± 25% of the area for an all *trans* sample. This estimate permits approximate resolution of $f(r)$ into *trans* and *gauche* components.

Once fairly good skeletal parameters are obtained, an estimate of the *trans* to *gauche* ratio can be obtained independently of the radial distribution approach by the correlation background method. Figure 5 indicates how much less sensitive the intensity is to variations in the concentrations of the isomers than to variations of a few tenths of a degree in the principal angles, as illustrated in Fig. 4. The background function appears to be smoother for the model with 55% *trans* than for 40% or 70%.

The method used in this investigation to obtain the most probable composition relied upon the radial distribution function. Experimental $f(r)$ curves were computed using models based on concentrations of 40% *trans*, 55% *trans* and 70% *trans*. Least squares cycles of the fits between comparable experimental and calculated $f(r)$ curves from r = 2.9 to 4.05 Å. were run until optimum structural parameters were obtained for all concentrations. The root-mean-square deviations between experimental and calculated curves were 0.0165, 0.0108 and 0.0118 for the 40, 55 and 70% concentrations, respectively. A parabolic fit of the deviations suggested that 60% *trans* was the most probable value, with an uncertainty of ±15%.

Representation of Experimental Intensity Data.—The advent of techniques yielding quantitative electron diffraction data raises the question of which graphical representation of experimental data most readily illustrates the quality of the work. Figure 6 presents the conventional comparison between calculated and observed reduced intensity curves. Figures 7 and 8 present an alternative comparison in terms of I_b instead of $M(q)_{\text{theor}}$. The nature and magnitude of flaws in the measured intensities are perhaps portrayed most strikingly in the latter curves. The conspicuous errors in intensity shown arise principally from flaws in the photographic emulsions, the instability of the recording microphotometer, imperfections in the chart paper and the judgment of the reader of the microphotome-

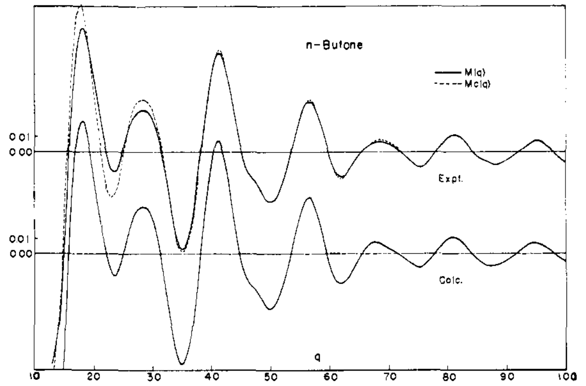

Fig. 6.—Reduced electron diffraction intensity curves. The solid lines represent the total scattering curves, $M(q)$, and the dashed line represents the experimental nuclear scattering curve, $M_c(q)$.

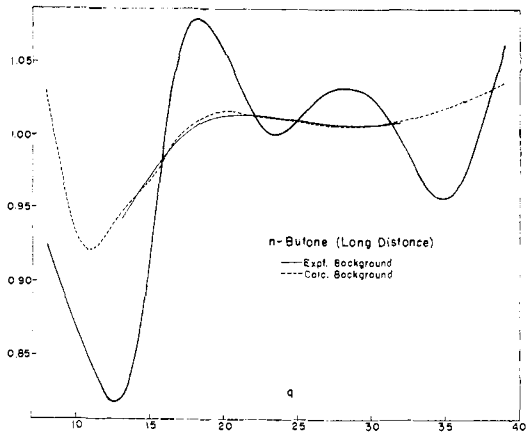

Fig. 7.—Experimental long camera distance intensity curve showing the background function used in computing $f(r)$ (solid line), and the correlation background function for a nearly optimum model (dashed line).

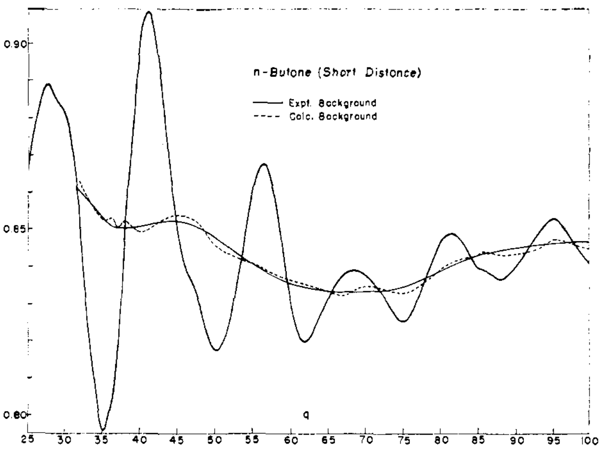

Fig. 8.—Experimental short camera distance intensity curve showing the experimental and computed background functions.

ter traces. The random errors in intensity in the present investigation are, unfortunately, severalfold larger than those obtained in the best of our recent work but nevertheless are appreciably smaller than those apparent in many sector-microphotometer investigations. Account is taken of these errors in assigning uncertainties.

It should be pointed out that the hump in the background line occurring at about $q = 20$ in the long camera distance patterns and at $q = 45$ in the short distance patterns arises because of the method of calibrating the sector shape and not from arbitrary judgment. The sector was calibrated using argon diffraction patterns and the hump seems to result from a discrepancy (less than 2%) between experimental and theoretical patterns. The hump is now well documented as it has appeared in the same place for the ten different molecules studied since the adoption of the argon calibration.

Discussion of Results

Whereas n-butane is one of the most significant molecules to study from the standpoint of rotational isomerization, it presents a much more difficult experimental problem than many molecules with terminal groups of greater electron scattering power. It is appropriate to analyze exhaustively the present experimental data for all information concerning internal rotation, even if the numbers obtained are somewhat crude, for electron diffraction gives quite the most direct geometrical picture of structure of any approach.

The parameters derived from the radial distribution curve are presented in Table I along with approximate standard (random intensity) errors discussed above. Over-all standard errors are also included which contain all known sources of error except those associated with the imperfectly understood uncertainties in the approximations of electron scattering theory. For an internal comparison internuclear distances are listed which are calculated from the four principal C–C and C–H peaks, assuming rigid *trans* and *gauche* isomers with $\phi = 180$ and $\pm 60°$, respectively. The deviations between the observed and calculated distances are within the limits of error of the experiment, but it is interesting to note that the deviations correspond to physically reasonable distortions from the reference model. If the assumptions (a) through (e) above about the structure are retained, it is possible to estimate the mean angles of twist about the 2–3 bond from the positions of the C_1--C_4 peaks.

For the *gauche* isomer the radial distribution curve suggests that ϕ is 63°. Although the standard deviation based on eq. 1 is only $\pm 3°$, it is more judicious to assign an uncertainty of $\pm 8°$, since the peak is not well separated from a broad C–H peak. The mutual avoidance of the terminal methyl groups, implied by the value of ϕ being greater than 60°, is demonstrated in the *gauche* to *trans* ratio, (n_g/n_t). From this ratio the energy difference, ΔE, between the isomers can be estimated from the simplified equation

$$n_g/n_t = 2 \exp(-\Delta E/RT) \qquad (2)$$

where the factor 2 is the statistical weight of the *gauche* isomer. Application of eq. 2, assuming $T \sim 287°$K.,[8] suggests that the *trans* form is more stable than the *gauche* form by 630 ± 350 cal./mole. The stated uncertainty reflects the 15% uncertainty in the concentration of the isomers, but the result is subject to an additional error of perhaps ±200 cal./mole owing to the assumption of unity for the ratio of the partition functions of the isomers. The energy difference may be compared with Pitzer's estimate of 800 cal./mole from heat capacity studies[3] of the gas molecules and with the value of 770 ± 90 cal./mole for liquid butane determined by Szasz, Sheppard and Rank[9] from the variation of Raman intensities with temperature. In azimuthal angle and in energy difference between isomers, n-butane ($\phi = 63 \pm 8°$, $60 \pm 15\%$ *trans*) appears to be intermediate between n-propyl chloride in which the terminal methyl and chloride groups appear to attract each other weakly and 1,2-dichloroethane

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(8) The initial temperature of the specimen was 305°K. Unfortunately, we have no reliable way of estimating the effect of expansion of the gas jet upon the effective temperature in our experiments. Our correction is possibly much too small. The associated uncertainty in ΔE, however, should be less than the others discussed.

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

where the repulsion between chlorine atoms is substantial in the *gauche* configuration. In electron diffraction studies,[7] Morino and Kuchitsu found for the former compound that $\phi = 59 \pm 5°$ with 19 ± 5% *trans* isomers and Ainsworth and Karle[10] determined the values $\phi = 71 \pm 5°$ with 73 ± 5% *trans* isomers for the latter compound.

The magnitude of the energy barrier separating the *trans* and *gauche* conformations has a yet smaller effect on the intensity of diffracted electrons than has the energy difference between the isomers. It is possible, nevertheless, to make a crude comparison of the diffraction results with the calorimetric results. If the potential energy of twist about the 2–3 bond is considered to be a perturbed ethane-like function given by $V_0(1 - \cos 3\theta)/2$ in the vicinity of the *trans* configuration, where V_0 is the potential barrier and θ is the azimuthal angle reckoned from the *trans* position, it is possible to estimate the probability distribution $P(\theta)$. Since the zero point energy of twisting is well under RT, the classical distribution

$$P(\theta) = A\exp(-V(\theta)/RT) \qquad (3a)$$

or, for small θ

$$P(\theta) \simeq A\exp(-9V_0\theta^2/4RT) = A\exp(\theta^2/2\theta^2_{\mathrm{rms}}) \qquad (3b)$$

should be reasonably accurate. The displacement of the C_1--C_4 internuclear distance from its value at $\theta = 0$ is proportional to θ^2 for small θ. The center of gravity of the *trans* probability distribution is therefore associated very nearly with the root-mean-square angle of twist from planarity. If V_0 is given the ethane value of 3 kcal./mole, it is seen that

$$\theta_{\mathrm{rms}} \simeq (2RT/9V_0)^{1/2} = 0.21 \text{ radian} = 12°$$

A more rigorous calculation of the diffraction parameter gives the same result. The experimental least squares angle of 13 ± 5° agrees pleasingly with the calculated angle but is not sufficiently reliable to establish the barrier to within narrow limits. Alternative comparisons based on the breadth and asymmetry of the C_1--C_4 peak appear to be outside the limits of reliability of the present data. It was found that the least squares fit of the thermal amplitude of vibration was a sensitive function of the assumed *trans* to *gauche* ratio.

The experimental root-mean-square amplitudes of vibration, l_{ij}, in Table I are seen to agree reasonably well with approximate values calculated by Morino, *et al.*,[11] for atomic pairs in given groups without regard to the specific molecules in which they appear.

The experimental parameters C–H = 1.108 ± 0.005 Å., C–C = 1.533 ± 0.003 Å. and C–C–H = 110.5 ± 0.7°, may be compared to similar parameters for ethane determined by electron diffraction by Almenningen and Bastiansen[12] who found 1.113 Å., 1.538 Å. and 109.5° (no uncertainties stated) and by Hedberg and Schomaker[13] who found 1.120 ± 0.03 Å., 1.538 ± 0.016 Å. and 110.5 ± 3.5°. The distances from the latter two investigations have been increased by $(l_{\mathrm{ij}}^2/r_{\mathrm{ij}})$ to correspond more nearly to our parameters, $r_g(0)$.[14] The spectroscopic parameters for ethane of 1.102 Å., 1.543 Å. and 109.6° reported by Hansen and Dennison[15] and for methane of C–H = 1.093 Å.[16] are averages over the ground vibrational state. The physical significance of the spectroscopic parameters in terms of centers of gravity may be uncertain by 0.01 Å. or more owing to the large stretching and bending amplitudes of vibration involving the hydrogen atoms. The butane carbon–carbon distances of 1.533 Å., 2.547 Å. and angle C–C–C = 112.4° are in excellent agreement with those determined by precise X-ray studies of some long chain crystalline hydrocarbons. Shearer and Vand[17] found 1.534 ± 0.006 Å., 2.546 ± 0.004 Å. and 112.2 ± 0.3° for n-$C_{36}H_{74}$. Smith[18] determined C---C to be 2.549 ± 0.004 Å. in n-$C_{23}H_{48}$. The agreement between n-butane and the other n-hydrocarbons through heptane is equally close.[6,19] The consistency of the results suggests that the 0.01 Å. difference between the C–C bond distance in n-hydrocarbons and the standard reference single bond distance of 1.544 Å. found in the diamond crystal[20] is real.

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[11] Y. Morino, K. Kuchitsu, A. Takahashi and K. Maeda, *ibid.*, **21**, 1927 (1953).

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[14] L. S. Bartell, *J. Chem. Phys.*, **23**, 1219 (1955).

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[16] For a summary of results see G. G. Shepard and H. L. Welsh, *J. Mol. Spectroscopy*, **1**, 277 (1957).

[17] H. M. M. Shearer and V. Vand, *Acta Cryst.*, **9**, 379 (1956).

[18] A. E. Smith, *J. Chem. Phys.*, **21**, 2229 (1953).

[19] It should be pointed out, however, that our C–C bond length is approximately 0.007 Å. shorter than that very recently determined for n-butane, also by electron diffraction, by Y. Morino and K. Kuchitsu who obtained results of apparently comparable internal consistency (private communication).

[20] K. L. Lonsdale, *Phil. Trans. Roy. Soc.*, **A240**, 1219 (1947).