

## MOLECULAR STRUCTURE OF *n*-BUTANE: CALCULATION OF VIBRATIONAL SHRINKAGES AND AN ELECTRON DIFFRACTION RE-INVESTIGATION

W. F. BRADFORD, SUSAN FITZWATER and L. S. BARTELL\*

*Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109 (U.S.A.)*

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### ABSTRACT

A normal coordinate analysis was carried out based on the force field of Schachtschneider and Snyder in order to calculate all amplitudes of vibration and shrinkage corrections for *n*-butane. The results are tabulated to aid diffraction analyses of related substances. A vapor-phase electron diffraction reinvestigation of *n*-butane led to experimental measurements of the principal amplitudes of vibration and to the following molecular parameters ( $\pm 3\sigma$ ):  $r_g(\text{C—C}) = 1.531(2)\text{Å}$ ,  $r_g(\text{C—H}) = 1.117(5)\text{Å}$ ,  $\angle \text{CCC}$  (*trans, gauche* average) =  $113.8(4)^\circ$ ,  $\angle \text{CCH}$  (ave) =  $111.0(5)^\circ$ , *gauche* CCCC dihedral angle  $65(6)^\circ$ , % *trans* conformer =  $54 \pm 9\%$ , and  $\Delta G^\circ$  (*gauche—trans*) =  $497 \pm 220 \text{ cal mol}^{-1}$ .

### INTRODUCTION

As part of a continuing program of research on hydrocarbon compounds we have reinvestigated the molecular structure of *n*-butane; it is the simplest alkane exhibiting *trans—gauche* rotational isomerization and, hence, is a prototype system for theories of conformational analysis. Although several prior structure determinations by the sector method have been reported [1, 2], they were carried out before it was feasible to perform a thorough normal coordinate calculation of the various vibrational corrections that enhance the analysis of structural information in electron diffraction studies. In addition, data acquisition and processing have improved materially since the last investigation of *n*-butane. In this paper we report a systematic listing of the important Bastiansen—Morino shrinkage corrections [3, 4] as well as structural parameters. We have found these shrinkages to be valuable in subsequent analyses of more complex systems.

### EXPERIMENTAL PROCEDURE

A sample of *n*-butane with a stated purity of 99.94 mole per cent was obtained from the Phillips Petroleum Company. It was transferred to a sample

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\* Author to whom correspondence should be addressed.

container by triple vacuum distillation and was used without further purification. Scattering patterns provided by 40 kV incident electrons were obtained at the 21- and 11-cm distances through a rotating  $R^3$  sector and at the 21-cm distance through a rotating  $R^2$  sector. The sample container was maintained at a temperature of  $-63.5^\circ\text{C}$  to provide a sample pressure of 30 torr [1 torr = (101.3/760) kPa]; the nozzle was maintained at room temperature (ca.  $30^\circ\text{C}$ ). Diffraction patterns were recorded on  $4 \times 5$  in. Kodak Electron Image plates in an apparatus described elsewhere [5]. Experimental conditions are summarized in Table 1.

Photographic densities,  $A$ , measured with an automated microphotometer [5], were converted to relative intensities,  $E$  via [6]

$$E = A(1 + 0.116A + 0.017A^2 + 0.00312A^3). \quad (1)$$

Intensities of five plates at each camera distance were averaged together and leveled in the conventional manner, using the partial wave elastic and inelastic scattering factors tabulated by Schafer, Yates, and Bonham [7]. The experimental  $s$  and leveled  $I_0(s)$  values, as well as the interpolated  $s$ ,  $I_0(s)$ , and background functions,  $I_B(s)$ , which were subsequently employed in the structure analysis are available as supplementary material.\*

## ANALYSIS OF DATA

### *Molecular model*

It was assumed that *n*-butane exists in two rotational configurations, *trans* and *gauche*, with relative concentrations to be determined. *Trans* and *gauche* isomers were assumed to have, respectively,  $C_{2h}$  and  $C_2$  symmetries with thermal excursions of the *trans* CCCC dihedral angle from  $180^\circ$  taken into account by shrinkage corrections [3, 4]. The *gauche* and *trans* isomers

\*The above information as well as the *n*-butane frequencies calculated in the course of a normal coordinate analysis is available as Sup. Pub. No. SUP 26054 (4 pages) from British Library Lending Division, Boston Spa, Wetherby, Yorkshire, LS23 7BQ.

TABLE 1

Experimental conditions under which diffraction patterns of *n*-butane were recorded

Camera geometry	I	II	III
Camera distance (cm)	21.094	21.158	10.919
Sector (radius, cm)	$r^2$ (3.2)	$r^3$ (4.8)	$r^3$ (4.8)
Sample temperature ( $^\circ\text{C}$ )	$-63.5$	$-63.5$	$-63.5$
Sample pressure (torr)	30	30	30
Exposure time (sec)	0.25–0.50	12.5	20.0
Beam current ( $\mu\text{A}$ )	0.756	0.686	0.728
Pt. nozzle throat diameter (cm)	0.028	0.028	0.028
Nozzle lip to beam distance (cm)	0.035	0.043	0.044
Electron wavelength ( $\text{Å}$ )	0.060153	0.060153	0.060153

were initially assumed to be identical in internal coordinates except for torsional angle and the set of shrinkages applied to the non-bonded distances of each. All C—C and C—H bond distances were assumed to be equivalent. No distinction was made between CCH angles of methyl and methylene groups. Since experience showed that the twist angle of the *gauche* methyl group could not be determined with useful precision, the value of this parameter was set at  $-2.5^\circ$ , as suggested by MUB-2 molecular mechanics calculations [8]. Accordingly, five independent structural parameters were refined. Five amplitudes of vibration were allowed to vary independently. These were the bonded C—C and C—H, the geminal C · · · C and C · · · H, and the 1 · · · 4 *gauche* C · · · C. Preliminary investigations showed that the 1 · · · 4 *trans* and *gauche* C · · · C amplitudes were sufficiently strongly correlated with the *trans* mole fraction that independent simultaneous refinements were unreliable. Because the *trans* concentration is of greater intrinsic interest and is known less accurately than the 1 · · · 4 *trans* C · · · C amplitude, the latter parameter was fixed at the value deduced from the normal coordinate calculations described below, as were all other amplitudes not referred to above. The Morse asymmetry constants for all internuclear distances were set equal to  $2.0 \text{ \AA}^{-1}$ .

#### *Shrinkage corrections*

In order to correct the electron diffraction data for shrinkages in internuclear distances arising from perpendicular amplitudes of vibration, a normal coordinate analysis for both the *trans* and *gauche* forms was performed with Hilderbrandt's computer program MSAV [9]. The general valence force constants of Schachtschneider and Snyder [10], adjusted to correct their torsional constant [11] were used with two sets of geometrical parameters. The first of these sets adopted the idealized structures of Schachtschneider and Snyder while the other consisted of bond angles and lengths closely resembling those reported in previous electron diffraction investigations [1, 2]. The vibrational frequencies calculated and the structural parameters used are listed with the supplementary material.

Amplitudes of vibration and the  $K_{ij}$  corrections necessitated by perpendicular amplitudes of vibration as explained by Morino et al. [3] were derived from the normal coordinate analysis. These  $K_{ij}$  values together with the internuclear distances  $(r_g)_{ij}$  imply  $\phi_\alpha$  bond angles in the mean structure which can serve in place of the equilibrium bond angles originally invoked in the definition of and computation of practical shrinkages as outlined by Kuchitsu and Cyvin [4]. The resultant shrinkage corrections and amplitudes of vibration computed for *n*-butane for the various internuclear distances are listed in Table 2. These distances are labeled according to atomic indices illustrated in Fig. 1.

TABLE 2

Calculated amplitudes and practical shrinkages for *n*-butane<sup>a</sup>

	Atom pair <sup>b</sup>	Amplitude	Shrinkage	$r_{ij}$	Atom pair	Amplitude	Shrinkage	$r_{ij}$
1,3 <sup>c</sup>	C <sub>1</sub> ...C <sub>3</sub>	0.0728	0.0095	(2.5)	C <sub>1</sub> ...H <sub>6</sub>	0.1088	0.0020	(2.2)
	C <sub>3</sub> ...H <sub>1</sub>	0.1097	0.0158	(2.2)	C <sub>1</sub> ...H <sub>7</sub>	0.1088	0.0055	(2.2)
	C <sub>3</sub> ...H <sub>2</sub>	0.1101	0.0115	(2.2)	H <sub>1</sub> ...H <sub>2</sub>	0.1275	-0.0002	(1.8)
	C <sub>3</sub> ...H <sub>3</sub>	0.1101	0.0074	(2.2)	H <sub>1</sub> ...H <sub>3</sub>	0.1275	0.0043	(1.8)
	C <sub>3</sub> ...H <sub>6</sub>	0.1090	0.0069	(2.2)	H <sub>2</sub> ...H <sub>3</sub>	0.1275	0.0025	(1.8)
	C <sub>3</sub> ...H <sub>7</sub>	0.1087	0.0029	(2.2)	H <sub>4</sub> ...H <sub>5</sub>	0.1280	0.0072	(1.8)
1,3	C <sub>1</sub> ...C <sub>3</sub>	0.0726	0.0051	(2.5)	C <sub>1</sub> ...H <sub>6</sub>	0.1088	0.0043	(2.2)
	C <sub>3</sub> ...H <sub>1</sub>	0.1097	0.0099	(2.2)	H <sub>1</sub> ...H <sub>2</sub>	0.1275	0.0051	(1.8)
	C <sub>3</sub> ...H <sub>2</sub>	0.1101	0.0095	(2.2)	H <sub>2</sub> ...H <sub>3</sub>	0.1275	0.0014	(1.8)
	C <sub>3</sub> ...H <sub>6</sub>	0.1092	0.0069	(2.2)	H <sub>4</sub> ...H <sub>5</sub>	0.1280	0.0059	(1.8)
1,4 <i>trans</i>	C <sub>1</sub> ...C <sub>4</sub>	0.0722	0.0265	(3.9)	H <sub>3</sub> ...H <sub>4</sub>	0.1294	0.0290	(3.1)
	C <sub>2</sub> ...H <sub>1</sub>	0.1065	0.0298	(3.5)	H <sub>4</sub> ...H <sub>7</sub>	0.1291	0.0289	(3.1)
	C <sub>1</sub> ...H <sub>5</sub>	0.1068	0.0283 <sup>c</sup>	(3.5)	H <sub>3</sub> ...H <sub>4</sub>	0.1294	0.0259 <sup>c</sup>	(3.1)
	C <sub>2</sub> ...H <sub>1</sub>	0.1066	0.0366 <sup>c</sup>	(3.5)	H <sub>4</sub> ...H <sub>4</sub>	0.1291	0.0288 <sup>c</sup>	(3.1)
					H <sub>2</sub> ...H <sub>5</sub>	0.1294	0.0313 <sup>c</sup>	(3.1)
1,4 <i>gauche</i>	C <sub>1</sub> ...C <sub>3</sub>	0.1849	0.0137 <sup>c</sup>	(2.9)	H <sub>4</sub> ...H <sub>6</sub>	0.1898	0.0059	(2.5)
	C <sub>1</sub> ...H <sub>4</sub>	0.1830	0.0041	(2.7)	H <sub>1</sub> ...H <sub>4</sub>	0.1886	0.0090 <sup>c</sup>	(2.5)
	C <sub>2</sub> ...H <sub>2</sub>	0.1845	0.0059	(2.7)	H <sub>2</sub> ...H <sub>4</sub>	0.1905	0.0064 <sup>c</sup>	(2.5)
	C <sub>1</sub> ...H <sub>3</sub>	0.1834	0.0099 <sup>c</sup>	(2.7)	H <sub>3</sub> ...H <sub>5</sub>	0.1905	0.0058 <sup>c</sup>	(2.5)
	C <sub>2</sub> ...H <sub>2</sub>	0.1845	0.0152 <sup>c</sup>	(2.7)	H <sub>5</sub> ...H <sub>7</sub>	0.1849	-0.0042 <sup>c</sup>	(2.5)
	C <sub>2</sub> ...H <sub>3</sub>	0.1847	0.0083 <sup>c</sup>	(2.7)	H <sub>3</sub> ...H <sub>7</sub>	0.1879	0.0014 <sup>c</sup>	(2.5)
	H <sub>2</sub> ...H <sub>4</sub>	0.1905	0.0075	(2.5)	H <sub>1</sub> ...H <sub>5</sub>	0.1885	0.0149 <sup>c</sup>	(2.5)
	H <sub>1</sub> ...H <sub>4</sub>	0.1886	0.0055	(2.5)				
1,5 <i>tg</i>	C <sub>1</sub> ...H <sub>1</sub>	0.1942	0.0458 <sup>c</sup>	(3.9)	H <sub>2</sub> ...H <sub>7</sub>	0.1943	0.0419 <sup>c</sup>	(3.7)
	( <i>gt</i> ) C <sub>1</sub> ...H <sub>2</sub>	0.1817	0.0352	(4.2)	H <sub>3</sub> ...H <sub>7</sub>	0.1945	0.0352 <sup>c</sup>	(3.7)
	( <i>tg</i> ) H <sub>1</sub> ...H <sub>6</sub>	0.1938	0.0413 <sup>c</sup>	(3.7)	H <sub>1</sub> ...H <sub>6</sub>	0.1911	0.0341	(3.7)
1,5 <i>tt</i>	C <sub>1</sub> ...H <sub>1</sub>	0.1215	0.0470	(4.7)	H <sub>1</sub> ...H <sub>7</sub>	0.1431	0.0513 <sup>c</sup>	(4.3)
1,5 <i>gg</i>	C <sub>1</sub> ...H <sub>2</sub>	0.2843	-0.0194 <sup>c</sup>	(2.6)	H <sub>2</sub> ...H <sub>6</sub>	0.2719	-0.0291	(2.5)
	C <sub>1</sub> ...H <sub>3</sub>	0.3295	0.0300 <sup>c</sup>	(3.3)	H <sub>2</sub> ...H <sub>6</sub>	0.3008	0.0308 <sup>c</sup>	(3.1)
	H <sub>3</sub> ...H <sub>6</sub>	0.2745	-0.0244 <sup>c</sup>	(2.5)	H <sub>2</sub> ...H <sub>7</sub>	0.3007	0.0203	(3.1)
1,6	H <sub>1</sub> ...H <sub>8</sub>	0.1427	0.0779	(5.6)	H <sub>2</sub> ...H <sub>10</sub>	0.1988	0.0654	(4.7)
	( <i>ttt</i> ) H <sub>1</sub> ...H <sub>9</sub>	0.2349	0.0480	(4.8)	( <i>gtg</i> ) H <sub>2</sub> ...H <sub>9</sub>	0.3553	-0.1029 <sup>c</sup>	(1.9)
	( <i>ttg</i> ) H <sub>1</sub> ...H <sub>8</sub>	0.2004	0.0843 <sup>c</sup>	(5.0)	( <i>ggg</i> ) H <sub>2</sub> ...H <sub>10</sub>	0.4595	-0.0033 <sup>c</sup>	(2.8)
	( <i>tgt</i> ) H <sub>1</sub> ...H <sub>9</sub>	0.3028	0.0188 <sup>c</sup>	(3.5)	( <i>ggg</i> ) H <sub>3</sub> ...H <sub>10</sub>	0.3835	0.0686 <sup>c</sup>	(4.0)
	( <i>ggt</i> ) H <sub>1</sub> ...H <sub>10</sub>	0.3570	0.0511 <sup>c</sup>	(4.1)	( <i>ggg</i> ) H <sub>3</sub> ...H <sub>9</sub>	0.4598	-0.0034 <sup>c</sup>	(2.8)
	( <i>ggt</i> ) H <sub>2</sub> ...H <sub>9</sub>	0.2825	0.0356	(4.3)	( <i>ggg</i> ) H <sub>3</sub> ...H <sub>8</sub>	0.3571	0.0512 <sup>c</sup>	(4.1)
	( <i>gtg</i> ) H <sub>2</sub> ...H <sub>8</sub>	0.3023	0.0189 <sup>c</sup>	(3.5)	( <i>ggt</i> ) H <sub>2</sub> ...H <sub>8</sub>			
	( <i>ggt</i> )							

<sup>a</sup>Units for shrinkages and internuclear distances are in Å; calculations based on idealized structure of ref. 10. Temperature, 300 K. Shrinkages subsequently calculated at 420 K were very nearly 420/300 times the 300 K shrinkages.

<sup>b</sup>Atom numbering is shown in Fig. 1.

<sup>c</sup>Shrinkages obtained from the *gauche* normal coordinate analysis; all others are from the *trans*.

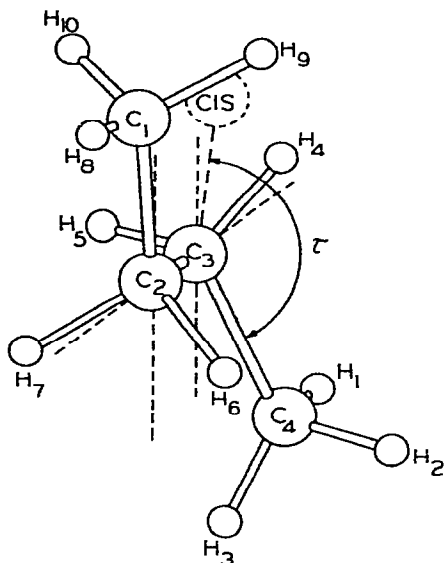


Fig. 1. Numbering scheme for atoms in *n*-butane.

#### Determination of structural parameters

After the intensity data sets from each camera distance were subjected to preliminary least squares refinements to arrive at background functions, the data from the various camera distances were blended to yield a molecular intensity curve ranging from  $s = 2.51$  to  $s = 39.58$ . A succession of least squares analyses of the intensity data was performed, adopting different values of the *gauche* fraction. The value chosen had a negligible effect upon the values derived for the independent parameters, but an appreciable effect upon the fit of the intensity function. The best value of the *gauche* fraction was taken to be that yielding the minimum value of  $\sigma(I)$  when  $s$ -weighted  $M(s)$  values were refined.

Analyses of intensity data were performed with both  $s$  and  $s^2$  weighting of the squared residuals. The most favorable weighting appeared to be intermediate between  $s$  and  $s^2$ , with the  $s$ -weighted residuals giving a somewhat more even distribution than did the  $s^{1/2}$ -weighted residuals. Somewhat arbitrarily, the value of the *gauche* fraction was determined from the  $s$ -weighted least-squares, while the structural and amplitude parameters were determined from the  $s^2$ -weighted least-squares. Fortunately, differences between structural and amplitude parameters determined from the two sets of analyses were negligible.

#### RESULTS

Figures 2 and 3 show the blended molecular intensity function for *n*-butane and the corresponding radial distribution function, respectively.

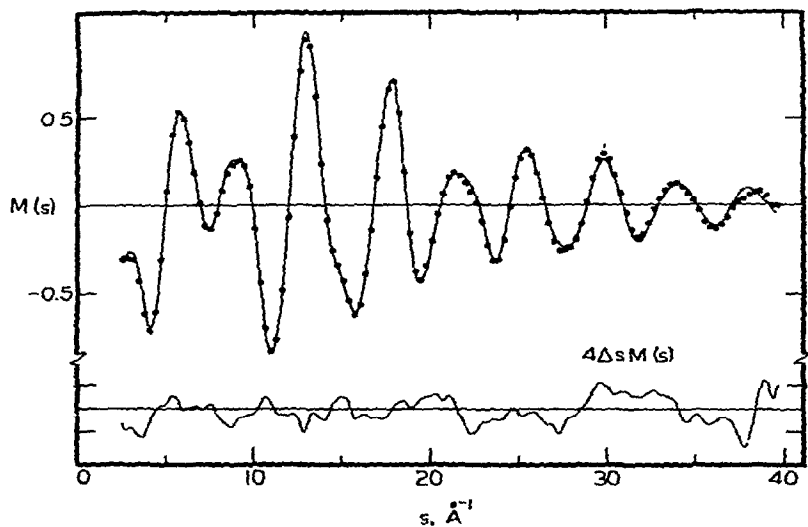


Fig. 2. Reduced intensity curves for *n*-butane and least-squares residuals. Points, experimental; solid line, calculated.

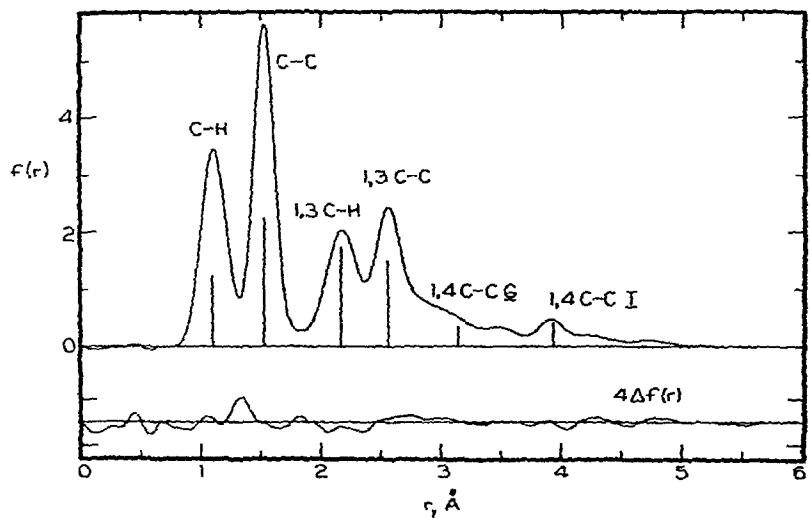


Fig 3. Experimental radial distribution curve for *n*-butane.

Values determined for the molecular parameters are listed along with their estimated limits of error in Table 3. Almost all quoted uncertainties correspond to three times the least-squares standard deviations corrected (approximately) for the effects of correlation of the intensities according to eqn. (2) of Bartell and Anashkin [12]. In the case of the *gauche* CCCC

TABLE 3

Molecular parameters and estimated errors ( $3\sigma$ ) for *n*-butane<sup>a</sup>

Parameter	$r_e^{\text{expt}}$	$l_e^{\text{expt}}$	$l_{\text{calc. b}}$
C—C	1.531(2)	0.0535(37)	0.051
C—H	1.117(5)	0.082(7)	0.079
1,3C . . . H	2.190(6)	0.112(9)	0.109
1,3C . . . C	2.558(5)	0.071(6)	0.072
1,4(C . . . C) <sub>G</sub>	3.135(40)	0.126(41)	0.185
1,4(C . . . C) <sub>T</sub>	3.912	(0.0722) <sup>c</sup>	0.0722
$\angle$ CCC		113.8(4)	
$\angle$ (CCH) <sub>AV</sub>		111.0(5)	
<i>gauche</i> dihedral angle		64.9(60) <sup>d</sup>	
% <i>trans</i> conformer = 53.5 ± 9%			
$\Delta G^\circ$ ( <i>gauche</i> — <i>trans</i> ) = 497 ± 220 cal mol <sup>-1</sup>			
Index of resolution	0.964	0.861	0.737
Camera dist. (sector)	11( $R^3$ )	21( $R^3$ )	21( $R^2$ )
$\sigma(I)/\langle I \rangle = 0.00086, s^2$ -weighting; 0.00109, $s$ -weighting			

<sup>a</sup>Distances in Å, angles in degrees. Uncertainties do not include uncertainties in calculated shrinkages or assumed asymmetry constants. They do include estimated error limits in scale factors of 1 part per thousand and in amplitudes of vibration of 6% due to various factors.

<sup>b</sup>Based in field of ref. 10 at 300 K.

<sup>c</sup>Fixed at calculated value. See text.

<sup>d</sup>Uncertainty subjectively amplified by a factor of 2.5 from least squares result.

from the standard deviation of the intensity as a function of mole fraction in accord with the relation

$$\sigma_I^2(\hat{X} + \sigma_x) = \sigma_I^2(\hat{X})\{1 + [B_{xx}(B^{-1})_{xx}/(n - m)]\}. \quad (2)$$

where  $\sigma_I(\hat{X})$  is the minimum value of  $\sigma(I)$ ,  $\sigma_I(\hat{X} + \sigma_x)$  is the value of  $\sigma(I)$  when the mole fraction has been displaced from its least-squares value  $\hat{X}$  by  $\sigma_x$  and  $B$  is the information matrix. The product  $B_{xx}(B^{-1})_{xx}$  was assumed to be 3 because of parameter correlations.

## DISCUSSION

The observed mole fraction of *trans* conformers of 53.5% implies a *gauche*—*trans* free energy difference of 497 cal mol<sup>-1</sup> if it is assumed that the effective sample temperature is 300 K after the free expansion of the gas from the nozzle to the electron beam. A limit of error of 9% in the

TABLE 4

Correlation matrix for *n*-butane<sup>a</sup>

$r_{C-C}$	$r_{C-H}$	$\angle HCC$	$\angle CCC$	$r_{CCCC}(G)$	$l_{C-C}$	$l_{C-H}$	$l_{1,3} C \dots C$	$l_{1,3} C \dots H$	$l_{1,4} C \dots C(G)$	$R^b$	
$\sigma^c$	0.429	0.931	0.173	0.131	0.972	0.487	0.928	1.37	1.79	17.7	0.00927
	1.000	0.049	-0.208	-0.389	0.030	0.067	0.045	0.035	0.002	-0.008	0.067
		1.000	-0.306	-0.014	0.051	0.130	0.162	0.058	0.034	0.002	0.199
			1.000	0.164	-0.221	-0.108	-0.105	-0.148	0.048	0.046	-0.161
				1.000	0.136	0.000	0.004	-0.022	0.162	0.007	0.014
					1.000	0.052	0.046	0.078	0.034	-0.122	0.079
						1.000	0.373	0.168	0.201	-0.010	0.681
							1.000	0.140	0.162	-0.008	0.553
								1.000	0.004	-0.019	0.254
									1.000	-0.001	0.296
										1.000	-0.014
											1.000

<sup>a</sup>From zero-order error matrix, notation of ref. 12, mole fraction *trans* fixed at 55%.<sup>b</sup>Index of resolution.<sup>c</sup>Zero-order standard deviations, distances *r* and *l* in thousandths of an Angstrom unit, angles in degrees, *R* dimensionless.



All of the molecular parameters found are in fair agreement with those reported in the earlier structural studies of vapor-phase *n*-alkanes [1, 2, 13, 15] except for the CCC bond angle. Our value for this angle,  $113.8^\circ$ , is slightly larger than the  $112.6^\circ$  average previously reported for a series of *n*-alkanes [13] (*n*-butane through *n*-heptane) a number of years ago. However, a recent study of *n*-hexadecane [16] has indicated an average CCC angle of  $114.6 \pm 0.6^\circ$ , and 2-fluoropropane has been reported to have an angle of  $114.6 \pm 1^\circ$  [17]. Part of the difference between the earlier and the present values of the CCC angle can be attributed to the shrinkage correction adopted in the present analysis (increasing the angle  $0.5^\circ$ ) and part is due to the nonbonded asymmetry constant,  $a = 2$  (which increases the angle by perhaps  $0.3^\circ$ ). The latter constant is quite speculative, even today. Not enough information is contained in the diffraction data to obtain independent values for the *gauche* and *trans* CCC angles. If the difference between them is fixed to be  $1.26^\circ$ , the value calculated by molecular mechanics with the MUB-2 force field [8], the remaining parameters refine to virtually the same values as they do with the difference set equal to zero.

The new results appear to be approximately twice as precise as those previously published [1, 2]. Although there is substantial agreement between the new bond lengths and the older ones for butane, and between the butane values and those of other short-chain *n*-alkanes, we have recently discovered that the C—C bond length is not as constant as it had once appeared to be. It increases in *n*-alkane chains by 0.01 Å upon going from an exterior  $\text{CH}_3\text{CH}_2$  or  $\text{CH}_3\text{CH}_2\text{—CH}_2$  bond to an interior  $\text{CH}_2\text{—CH}_2$  bond in a long chain. The evidence for this is presented elsewhere [16].

#### ACKNOWLEDGEMENTS

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