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Molecular Structure of Propane

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The structure of propane has been investigated by gas electron diffraction. The thermal average distances r_g and r_α-angles determined with the estimated limits of error were: C–C=1.532±0.003 Å, C–H=1.107±0.005 Å, ∠CCC=112±1°, and ∠HCH(CH_3)=107±3°. By combining the diffraction results with the microwave data, the zero-point average structure has also been determined.

The structures of ethane and four *n*-hydrocarbons from butane to heptane were previously determined by gas-phase electron diffraction.[1,2] Somehow propane has been missing in this group of diffraction data. Lide investigated the microwave spectra of propane and its isotopic species,[3] and determined the substitution coordinates and the structure parameters. However, the C–C distance 1.526 Å he obtained was outside the range of the thermal average C–C distances 1.531—1.534 Å, of other *n*-hydrocarbons determined by electron diffraction, beyond the stated uncertainties. As was commented by Lide himself,[4] the existence of this difference was not surprising, in view of the different nature of the averaging over vibrational motions.

The present study was initiated for the purpose of filling up the list of the structure data of simple *n*-hydrocarbons. The C–C r_g distance has been determined to be 1.532±0.003 Å. Further by applying an appropriate correction for the vibrational effect, the microwave data have been combined with the diffraction result, and the structure parameters have been determined for the zero-point average configuration.

Electron Diffraction

The diffraction photographs were taken and analyzed by our routine procedures of recent sector-microphotometer method.[5] Experimental conditions were as follows: accelerating voltage was 42 kV, camera distance 109.3 mm, beam current 0.1 μA, and exposure time 4 min. Carbon disulfide was used as the reference substance. The results of the least-squares analysis for three best plates are summarized in Table 1. The indices of resolution were 0.94—0.98. All the nonbonded distances other than listed in the table were restricted under the geometrical constraint of r_a parameters. The HCH angle of the methylene group was assumed to be 106.1°, the value given by Lide.[3] The

TABLE 1. RESULTS OF THE LEAST-SQUARES ANALYSIS OF PROPANE (in Å units)[a]

	r_{C-C}	$r_{C\cdots C}$	r_{C-H}[b]	$r_{C\cdots H}$[c]
r_a	1.5307	2.5421	1.1017	2.1886
σ_1	10	58	19	94
σ_2	6	21	2	26
r_g	1.5323	2.5440	1.1073	2.1940
limit of error	30	150	51	245
r°_α (r_z)[d]	1.5307	—	1.0956 (CH_3) 1.0941 (CH_2)	—

ϕ_α (CCC) 112.4°±1.2°, ϕ_α (HCH; CH_3) 107°±3°
ϕ_α (HCH; CH_2) 106.1° (assumed)

a) Errors are in 10^{-4} Å units.
b) The r_a values of the methyl and the methylene C–H distances were assumed to be equivalent.
c) $r_{C\cdots H}$ is the distance between the central carbon atom and one of the methyl hydrogens.
d) Morse parameters were assumed to be 2.1 $Å^{-1}$ for C–C and 1.98 $Å^{-1}$ for C–H, respectively. The centrifugal stretching was assumed to be 0.0002 Å for C–C.

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[1] L. S. Bartell and H. K. Higginbotham, *J. Chem. Phys.*, **42**, 851 (1965).

[2] a) R. A. Bonham and L. S. Bartell, *J. Amer. Chem. Soc.*, **81**, 3491 (1959); b) R. A. Bonham, L. S. Bartell, and D. A. Kohl, *ibid.*, **81**, 4765 (1959); c) K. Kuchitsu, This Bulletin, **32**, 748 (1959).

[3] D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1514 (1960).

[4] D. R. Lide, Jr., *ibid.*, **33**, 1519 (1960).

[5] *e.g.*, S. Konaka and M. Kimura, This Bulletin, **43**, 1693 (1970).

C_{2v} symmetry of the whole molecule and the C_{3v} symmetry of the methyl tops were assumed. The conformation of the methyl hydrogens was taken as determined by Lide,[3] namely, the in-plane hydrogen is in the *trans* position to the C–C bond. All the mean amplitudes were fixed at the calculated values.

The present least-squares analysis did not follow an orthodox constrained procedure[6] but a more simplified method was employed. The four independent parameters were adjusted by the ordinary non-constrained least-squares routine, the dependent parameters being fixed. The dependent parameters were, however, recomputed and reset at every cycle of the least-squares iteration, by the use of the new values of the independent parameters. This method is practically useful but the standard deviations might be slightly larger than the values the exact constrained procedure would give.

The observed and calculated molecular intensity curves are shown in Fig. 1.[7]

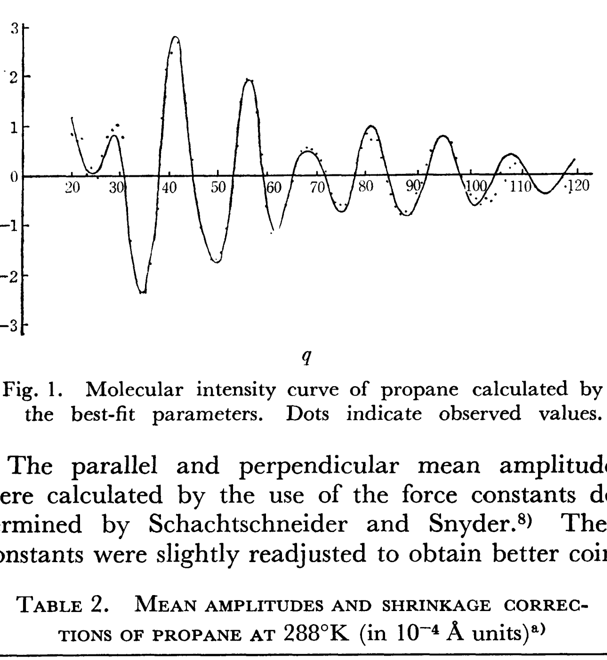

Fig. 1. Molecular intensity curve of propane calculated by the best-fit parameters. Dots indicate observed values.

The parallel and perpendicular mean amplitudes were calculated by the use of the force constants determined by Schachtschneider and Snyder.[8] Their constants were slightly readjusted to obtain better coincidence between the calculated and observed frequencies, because the structure parameters of the present study were not exactly the same as their values. Furthermore, the torsional constants were so adjusted as to give the frequencies determined by Hirota, Matsumura, and Morino.[9] For this purpose, an additional force constant which couples the two of the torsional internal coordinates had to be introduced. The calculated values of the mean amplitudes and the nonlinear shrinkage correction Δ are listed in Table 2. The quantity $\Delta = r_a - r_\alpha$ was given by $(\langle \Delta\rho^2 \rangle - 2\, l^2)/2r$, where $\langle \Delta\rho^2 \rangle$ is the perpendicular mean amplitude of the atom pair concerned.[10]

TABLE 2. MEAN AMPLITUDES AND SHRINKAGE CORRECTIONS OF PROPANE AT 288°K (in 10^{-4} Å units)[a]

	l	Δ[b]		l	Δ[b]
C_1–C_2	496	4	$H_4 \cdots H_5$	1299	78
$C_2 \cdots C_3$	698	−15	$H_6 \cdots H_7$	1283	355
$C_2 \cdots H_6$	786	249	$H_4 \cdots H_6$	1783	59
C_1–H_4	793	93	$H_4 \cdots H_7$	1854	19
$C_1 \cdots H_6$	1087	110	$H_4 \cdots H_8$	1303	71
$C_2 \cdots H_9$	1036	45	$H_6 \cdots H_9$	1414	87
$C_2 \cdots H_{10}$	1691	−12	$H_7 \cdots H_{10}$	2448	2
$C_2 \cdots H_4$	1075	20	$H_6 \cdots H_{10}$	1784	32
			$H_7 \cdots H_{11}$	2791	−244

a) The numbering of atoms are as follows: $C_1H_{4,5}$, methylene; $C_2H_{6,7,8}$, one methyl top; $C_3H_{9,10,11}$, the other methyl top. H_6 and H_9 lie on the CCC plane. H_7, H_4, and H_{10} are above the plane.

b) $\Delta = r_a - r_\alpha$.

Zero-point Average Structure

The effective moments of inertia of the normal species were converted to the zero-point moments of inertia, by applying the vibrational correction. The procedure has been established for ordinary molecules.[11] In the present study, the calculation was performed by an extended method applicable to a molecule containing internal rotors.[12] However, a recent investigation has revealed that the method used in the present study is not very exact but that a term proportional to the angular velocity of torsional motion should be added to the Eckart and Sayvetz conditions.[13] According to the rigorous treatment of a one-top problem the error due to the neglect of this term is of the order of 0.03 amu Å^2 for acetaldehyde.[13] Such an amount of error is not serious in the determination of the structure parameters with accuracy of 0.1% or so.

By assuming boldly that the same situation holds for propane, the zero-point average structure was de-

TABLE 3. MOMENTS OF INERTIA OF PROPANE (in amu Å^2 units)

	I_{obs}[a]	ΔI[b]	I_z[c]
a	17.3080	0.0634	17.371
b	59.8540	0.1053	59.959
c	67.7748	0.0427	67.818

a) Values observed by Lide.[3]

b) Correction for the vibrational effect.

c) Zero-point moments of inertia. $I_z = I_{obs} + \Delta I$.

TABLE 4. ZERO-POINT AVERAGE STRUCTURE OF PROPANE (r_z in Å, I in amu Å^2 units)

r_z(C–C)	1.533_7	∠CCC	112.0°
r_z(C–H)(CH_3)	1.097_6	∠HCH(CH_3)	107.9°
r_z(C–H)(CH_2)	1.096_2	∠HCH(CH_2)	107.8°

$I_z(obs) - I_z(calc)$

a	+0.02	*b*	−0.02	*c*	0.00

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[6] K. Hedberg and M. Iwasaki, *Acta Crystallogr.*, **17**, 529 (1964).

[7] Numerical experimental data of the leveled total intensity have been deposited with the Chemical Society of Japan (Document No. 7205). A copy may be secured upon request.

[8] J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963).

[9] E. Hirota, C. Matsumura, and Y. Morino, This Bulletin, **40**, 1124 (1967).

[10] Y. Morino, S. J. Cyvin, K. Kuchitsu, and T. Iijima, *J. Chem. Phys.*, **36**, 1109 (1962).

[11] a) Y. Morino, K. Kuchitsu, and T. Oka, *ibid.*, **36**, 1108 (1962); b) K. Kuchitsu, *ibid.*, **49**, 4456 (1968).

[12] T. Iijima and M. Kimura, Annual Meeting of the Chemical Society of Japan, Tokyo (April, 1970).

[13] T. Iijima, S. Tsuchiya, and M. Kimura, *ibid.*, Tokyo (October, 1971).

termined from both moments of inertia given in Table 3 and the diffraction results in Table 1. The r_α^0 or r_z distances, C–C, C–H(CH_3), and C–H(CH_2) were varied along the direction of the possible uncertainty of the scale factor. For each set of these distances, the remaining structure parameters, $\angle$HCH(CH_3), $\angle$HCH(CH_2), and $\angle$CCC can be determined from the three moments of inertia. Thus further judgment for the reasonableness of the obtained set was made by requiring that the $\angle$HCH(CH_3) and $\angle$CCC should not be outside the rather large limits of error of the ϕ_α angles given by the diffraction results.

The best set of the structure parameters thus obtained are shown in Table 4. The uncertainties of the parameters are roughly assessed to be 0.2%.

It should be noted that the average structure of Table 4 corresponds to the state where the torsional motion is frozen. Therefore the mean amplitude corrections applied to obtain r_α^0 from r_g were calculated without the torsional freedom, while the amplitude-quantities listed in Table 2 include the torsional motion as well as the vibrational motions.

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