actions broaden rather than double the band in water at high dilutions.

**Dioxane.**—The displacement to lower frequency of the C-O stretching mode in the dioxane spectrum upon the addition of water would indicate that hydrogen bond formation is occurring at this site. This is reasonable since the dioxane molecule has large dipole moments at the oxygen nuclei, even though it has essentially an over-all moment of zero. The reason for the high frequency shift of the modes involving the protons (C–H stretch and deformation) is not clear at this time. Since the shift to a higher frequency of the C–H stretching band is in an opposite direction to that expected as a result of hydrogen bonding, another phenomenon is apparently responsible. It may be a change in the ionic character of the C–H bond as dioxane becomes solvated, or coupling between the various vibrational modes may cause a disturbance of the C–H frequency when solvation occurs at the neighboring dioxane oxygen.

The infrared displacement curves in Fig. 2 show a sharp decrease in slope at high water concentrations. This is similar to the n.m.r. concentration dependent curve of the chemical shift for dioxane, which also leveled off and remained constant at dioxane concentrations less than ~30%. As stated previously,[2] this points to a local dioxane environment which is undergoing little or no change at high water concentrations.

Since the concentration dependence of the infrared and n.m.r. solvent shifts were somewhat similar, an attempt was made to correlate the results of the two techniques. The n.m.r. shifts were plotted vs. the infrared shifts observed at the same concentrations. Only vibrational modes involving the dioxane protons were used. These plots are illustrated in Fig. 4. In the case of the C–H bending modes, reasonably linear plots are obtained for all lines, whereas smooth curves are observed for the stretching frequencies. It is conceivable that a dipole moment change in a dioxane C–H bond, as well as a disturbance of the shielding of the proton involved, could result from a change in the electronic charge distribution of the C–H bond brought about by solvent interactions.

**Pyridine.**—The nuclear magnetic resonance results on pyridine–water mixtures[2] revealed that in addition to the interactions occurring at the nitrogen site, the β- and γ-protons also showed marked activity, indicated by their chemical shift concentration dependence. Unfortunately, the contributions from the chemically nonequivalent protons of pyridine cannot be distinguished in the infrared. The observed shifts were all toward higher frequencies as water was added. As with dioxane, the cause of the shifts to higher frequencies is uncertain, but similar phenomena may be operative in this molecule.

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# Electron Diffraction Determination of the Molecular Structure of the Butyl Halides. III. t-Butyl Chloride in the Gas Phase[1]

BY F. A. MOMANY, R. A. BONHAM, AND M. L. DRUELINGER

The structure of gaseous t-butyl chloride has been determined by the sector-microphotometer method of electron diffraction. The experimental molecular parameters were found to be: $r_g$(C–H) = 1.104 Å., $r_g$(C–C) = 1.532 Å., and $r_g$(C–Cl) = 1.828 Å.; $l_m$(C–H) = 0.075 Å., $l_m$(C–C) = 0.056 Å., and $l_m$(C–Cl) = 0.054 Å.; ∠C–C–Cl = 107.4° and ∠C–C–H = 110.0°. An approximate value of 4 kcal./mole was obtained for the barrier to rotation of the methyl groups about the C–C single bonds.

The structure of t-butyl chloride is of special interest because of the possibility that structural abnormalities might occur. In a previous study of t-butylacetylene and t-butyl cyanide, Nugent, Mann, and Lide[2] found a lengthening of the C–C bond connected to the t-butyl group of about 0.035 Å. Lide and Mann have also shown similar lengthenings in bonds connected to t-butyl groups in the cases of isobutane and t-butyl fluoride.[3]

The structure of t-butyl chloride has been worked out previously by a number of other investigators,[4-7] but none of these determinations has been of sufficient accuracy to give really definitive answers to the possibility of distortions in the structural parameters. It is also of interest to attempt to determine the barrier to rotation of the methyl groups about the carbon–carbon single bonds.

(1) The authors wish to thank the National Science Foundation and the Atomic Energy Commission for their financial support of this work.

(2) L. J. Nugent, D. E. Mann, and D. R. Lide, Jr., J. Chem. Phys., **36**, 965 (1962).

(3) D. R. Lide and D. E. Mann, ibid., **29**, 914 (1958).

(4) (a) O. Bastiansen and L. Smedvik, Acta Chem. Scand., **7**, 653 (1953); (b) J. W. Coutts and R. L. Livingston, J. Am. Chem. Soc., **75**, 1542 (1953).

(5) H. J. M. Bowen, A. Gilchrist, and L. E. Sutton, Trans. Faraday Soc., **51**, 1341 (1955).

(6) J. Y. Beach and D. P. Stevenson, J. Am. Chem. Soc., **60**, 475 (1938).

(7) J. Q. Williams and W. Gordy, J. Chem. Phys., **18**, 994 (1950).

## Experimental

A sample of t-butyl chloride was obtained from the Columbia Chemical Co. and was purified by vacuum column distillation. Boiling point and index of refraction measurements indicated the sample used for diffraction measurements was at least 99% pure. The sample of t-butyl chloride was purified immediately prior to the taking of the electron diffraction photographs in order to avoid any possible contamination. Electron diffraction photographs were obtained with an $r^3$ sector, using the sector electron diffraction camera in L. S. Bartell's laboratory at Iowa State University. Specimen pressures of 20 to 80 mm. with exposure times of 1 to 4 sec. were used at a temperature of 298°K. The beam current was 0.3 μa. and the accelerating voltage was 40 kv. Four research grade plates at each of two camera distances were obtained. The photograpic plates were microphotometered in Professor L. O. Brockway's laboratory at the University of Michigan.

The microphotometer traces of the electron diffraction photographs were read, at 0.25-mm. intervals, to four significant figures in the optical density with the aid of a Bausch and Lomb 7-power measuring magnifier. The photographic emulsion was calibrated by a procedure developed by Bartell and Brockway.[8] The indices of resolution were found to be 0.90 for the 21.35-cm. camera distance and 1.00 for the 10.66-cm. camera distance. It was felt that the near unity values of the indices of resolution indicated the absence of any serious extraneous scattering effects.

**Structure Analysis.**—The experimental data were analyzed according to numerical schemes outlined in detail elsewhere.[9-12]

(8) L. S. Bartell and L. O. Brockway, J. Appl. Phys., **24**, 656 (1953).

(9) R. A. Bonham and L. S. Bartell, J. Chem. Phys., **31**, 702 (1959).

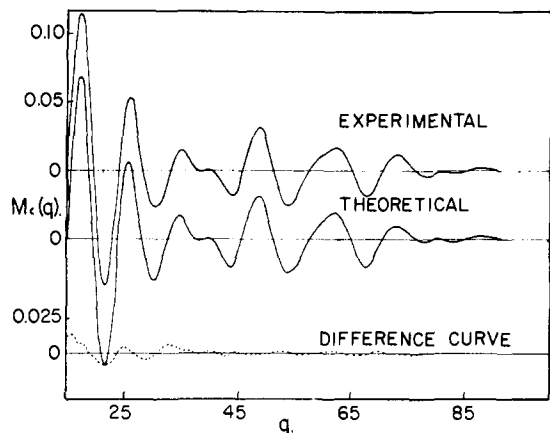(10) R. A. Bonham and T. Ukaji, ibid., **36**, 72 (1962).

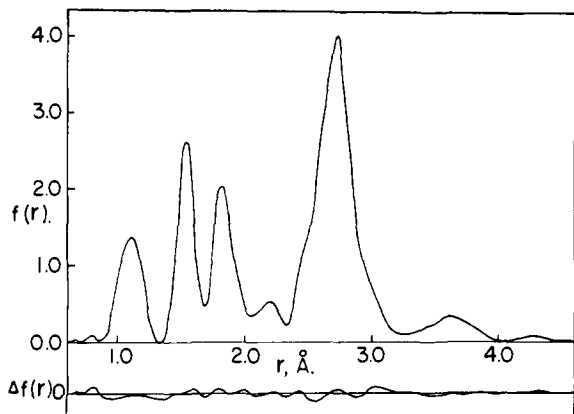Fig. 1.—Experimental and theoretical reduced molecular intensity curves and their difference.



Fig. 2.—Experimental radial distribution curve and the dfi-ference, $\Delta f(r)$, between it and the best theoretical model.

It was assumed that the hydrogen atoms were related by a three-fold axis of rotation about the carbon–carbon single bonds. Also, all of the C–C and C–H bonded distances, and Cl–C–C and C–C–H bond angles were assumed to be equivalent. These assumptions mean that if the assumed equivalences break down, the values reported in our analysis would refer to a measure of the average value of the parameter in question. The analysis employed in this work included corrections for anharmonicity of bonded distances, corrections for series termination effects, and corrections for failure of the Born approximation. The molecular parameters obtained by least squares analysis of the radial distribution curve were checked by use of the correlation method using the intensity curve.

The radial distribution curve used in the least squares analysis was obtained by Fourier sine transformation of the experimental intensity curve with a background function determined by use of the smoothness and Karle's nonnegative area criteria.[13] A con-vergence factor of the form $e^{-dq^2}$ with $d = 0.00211$ was used to decrease the effects of series termination errors. In the region $0 \leqq q \leqq 14$, both $M(q)$ data from a theoretical model and data generated from the experimental data[11] were employed.

## Results

The results of the final analysis for all the measured molecular parameters are given in Table I. The quoted uncertainties include estimates of experimental errors from various measured quantities and the ap-proximate errors in the measured parameters due to random errors in the data, but do not include possible sources of error from use of the kinematic scattering theory. In Fig. 1, the theoretical and experimental $M(q)$ curves and their differences are shown. Figure 2 presents similar results for the radial distribution curves. In Fig. 3 and 4, the long and short camera distance intensity curves and background functions are shown.

(11) R. A. Bonham and F. A. Momany, J. Phys. Chem., in press.
(12) M. Traetteberg and R. A. Bonham, submitted for publication.
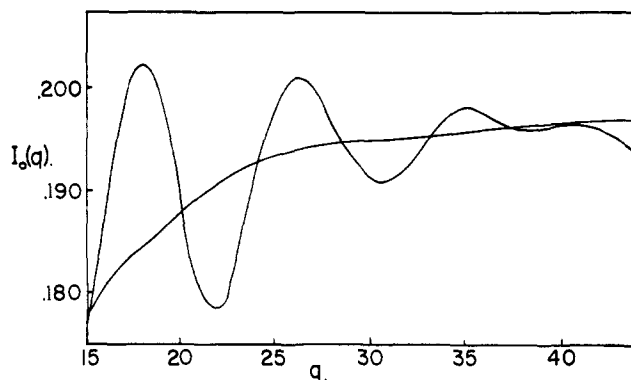(13) I. L. Karle and J. Karle, J. Chem. Phys., 17, 1052 (1949).

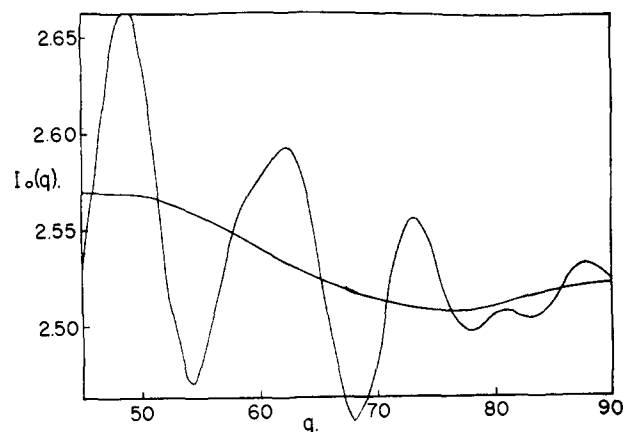Fig. 3.—Long camera distance intensity data and the back-ground.



Fig. 4.—Short camera distance intensity data and the back-ground.

The positions of the methyl groups were determined by using the correlation method with the intensity curve. It was found that the methyl groups were all in staggered ethane-like configurations and that any distortion from these configurations must be less than a 5° rotation about the C–C bond from the equilibrium positions of the ethane configuration.

TABLE I

MOLECULAR PARAMETERS AND UNCERTAINTIES FOR $t$-BUTYL CHLORIDE

| Peak | $r_g(0)$ | $\delta r$ | $l_{ij}$ exp | $\delta l_{ij}$ |
|------|----------|------------|--------------|-----------------|
| C–H | 1.104 | ±0.007 | 0.075 | ±0.010 |
| C–C | 1.532 | ± .006 | .056 | ± .007 |
| C–Cl | 1.828 | ± .010 | .050 | ± .006 |
| $C_{tert}$—H | 2.184 | ± .010 | .105 | ± .012 |
| $C_{Me}$—$C_{Me}$ | 2.540 | ± .010 | .075 | ± .010 |
| $C_{Me}$—Cl | 2.719 | ± .008 | .075 | ± .010 |
| Cl—$H_{trans}$ | 3.697 | ± .013 | .105 | ± .015 |
| ∠Cl–C–C | 107.4 ± 0.2° | | | |
| ∠C–C–H | 110.0 ± 0.5° | | | |

In Table II, the results are compared with the results found for related molecules. The lengthening of the C–Cl bond going from methyl to $t$-butyl appears to be 0.047 ± 0.010. This result appears to be similar to that found in the fluoride compound[3] which is 0.045 ± 0.015.

It was also possible in this analysis to determine a rough estimate to the barrier to rotation of the methyl groups. By making use of a method of Karle[14] and the measured amplitudes of the nonbonded distance between the chlorine atom and the three farthest hydrogens, and the methyl carbons to the neighboring *gauche* hydrogens, the barrier can be estimated to be

(14) J. Karle, ibid., 15, 202 (1947).

Table II

Structural Parameters for t-Butyl Chloride and Related Molecules

| Molecule, t-butyl | $r_{C-X}$, Å. | $r_{C-C}$, Å. | $r_{C-H}$, Å. | ∠Cl-C-C | ∠C-C-H | Method | References |
|---|---|---|---|---|---|---|---|
| Chloride | 1.828 | 1.532 | 1.104 | 107.4° | 110.0° | ED[a] | Present study |
| Chloride | 1.803 | 1.530 | | 108.1° | | MW[b] | c |
| Chloride | 1.80 | 1.54 | | 107.5° | | ED | 4b |
| Chloride | 1.80 | 1.54 | 1.10 | 107.0° | | ED | 4a |
| Chloride | 1.765 | 1.55 | 1.09 (ass.) | | 109° 28′ (ass.) | ED | 5 |
| Chloride | 1.78 | 1.54 (ass.) | 1.093 (ass.) | 109° 28′ | 109° 28′ (ass.) | MW | 7 |
| Fluoride | 1.43 | 1.525 | | | | MW | 3 |
| Acetylene | 1.495 | 1.532 | | 108.11° | | MW | 2 |
| Cyanide | 1.495 | 1.532 | | 108.42° | | MW | 2 |

[a] Electron diffraction. [b] Microwave spectroscopy. [c] D. R. Lide, Jr., and M. Jen, J. Chem. Phys., 38, 1504 (1963).

$4 \pm 2$ kcal./mole. The large uncertainty is mainly due to the fact that the amplitude of vibration for the methyl carbon to *gauche* hydrogen, on a neighboring methyl group, interaction cannot be determined with any great degree of reliability. The barrier is, however, in agreement with values reported for similar compounds.[3,15,16]

The C-C-Cl bond angle of 107.4° found in this investigation is in excellent agreement with the results of the most recent previous electron diffraction work.[3,4,5] The extra long C-Cl bond value has led us to consider other possible sources of error in the analysis. About the only impurity that could cause a shift in the C-Cl bond would be $Cl_2$, but it would take a 4.25% molar concentration of this molecule to shift an $r_{C-Cl}$ distance of 1.806 Å. to the reported 1.828 value. This would also require an 8.5% conversion of t-butyl chloride to another form and it is hard to imagine how this could take place without causing observable distortions in the carbon skeleton parameters. It also does not seem that $Cl_2$ would, in fact, even be the most likely decomposition product under the conditions of the experiment. In summary, since all the bonded peak areas checked with the theoretical values to less than 1%, it does not appear that the present results for the C-Cl bond length could be due to the presence of an impurity.

It would seem that a simple steric argument could easily account for the observed lengthening of the C-Cl

bond. The C-C bond lengths do not have to change appreciably as the strain imposed by the presence of the Cl is diluted somewhat among the three methyl groups, and a change in the C-C-Cl angle could account for the rest. The chlorine can only relieve the strain by moving away from the tertiary carbon atom. This change should, of course, lead to an increase in the bond moment of the C-Cl bond. It is of interest to note that regardless of what the correct interpretation of this phenomenon is, there seems to be an experimental rule of thumb that, in structures of the type considered here, the unique bond length always increases. This was shown first by Swick, et al.,[17] in hexachloroethane, and additional evidence in support of this result has been obtained from a recent redetermination of hexachloroethane by Traetteberg.[18] She has shown that the carbon–carbon bond, in this molecule, has been elongated by 0.031 Å. while the $-CCl_3$ groups appear to be normal except for slight angle changes.

(15) K. S. Pitzer and J. E. Kilpatrick, Chem. Rev., 39, 435 (1946).

(16) J. G. Aston, R. M. Kennedy, and S. C. Schumann, J. Am. Chem. Soc., 62, 2059 (1940).

(17) D. A. Swick, I. L. Karle, and J. Karle, J. Chem. Phys., 25, 1242 (1954).

(18) M. Traetteberg, Acta Chem. Scand., in press.

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# Electron Diffraction Determination of the Molecular Structure of the Butyl Halides. IV. The Structure and Conformational Analysis of n-Butyl Bromide in the Gas Phase[1a]

By F. A. Momany,[1b] R. A. Bonham,[1b] and W. H. McCoy[1c]

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The structure and conformational analysis of gaseous n-butyl bromide has been carried out by the sector-microphotometer method of electron diffraction. The molecular parameters for the bonded distances were found to be: $r_g$(C-H) = 1.101 Å., $r_g$(C-C) = 1.532 Å., and $r_g$(C-Br) = 1.950 Å.; $l_m$(C-H) = 0.071 Å., $l_m$(C-C) = 0.051 Å., and $l_m$(C-Br) = 0.050 Å.; and ∠C-C-C = 112.4°, ∠C-C-Br = 111.0°, and ∠C-C-H = 110.0°. The distribution of conformers at room temperature was found to be the same as the distribution for n-pentane. This gives identical energy differences favoring the *trans* forms at each end of the molecule by 650 cal./mole.

This work is the first attempt to obtain a complete structure determination of n-butyl bromide.[2a,b] It is therefore of interest to obtain precise values of the

bonded parameters for comparison with other similar halogen-substituted molecules. In view of the fact that both fluorine and chlorine stabilize *gauche* conformations,[3-5] it is also of interest to determine to what

(2) (a) R. J. W. LeFevre, R. Roper, and A. J. Williams, Australian J.
Chem., 12, 743 (1959); (b) Yu. A. Pentin and V. M. Taterskii, Doklady Akad. Nauk SSSR, 108, 290 (1956).

(3) Y. Morino and K. Kuchitsu, J. Chem. Phys., 28, 175 (1958).

(4) T. Ukaji and R. A. Bonham, J. Am. Chem. Soc., 84, 363 (1962).

(5) E. Hirota, J. Chem. Phys., 37, 283 (1962).