Dinitrophenols as Indicators.—In earlier work[3d] the equilibrium constant for association of triethylamine with benzoic acid in benzene was determined indirectly at 25°, using both bromophthalein magenta E and 2,5-dinitrophenol as indicators. By the criterion of association with triethylamine, these two indicators are, respectively about seven times as strong and one-tenth as strong as benzoic acid in this solvent.[20] A third determination of the same association constant was made with the aid of 2,4-dinitrophenol, whose strength (see Table II) more closely matches that of benzoic acid in benzene. From combined absorbance data at 350 and 400 mμ for 22 mixtures the value obtained was 3.64×10^3, with a relative standard deviation of $\sim 5\%$. A correction was applied as before[3d] for the monomer-dimer equilibrium of benzoic acid, which is the only competing association believed to be of significance in the systems being considered.[21] This belief is strengthened by the close agreement of the three results.

From this and the preceding[1] study, it seems evident that with the aid of suitable indicator acids the relative strengths of acids without visible color can be determined in a broad range of aprotic solvents, not merely in those solvents considered most suitable for infrared measurements (carbon tetrachloride, chloroform) or ultraviolet measurements (heptane, cyclohexane and the like).

Selection of Reference Base.—It is clear that the results of investigations will depend to some extent on the choice of *reference base*. Previous studies have demonstrated characteristic differences in the behavior of primary, secondary and tertiary aliphatic amines in aprotic solvents.[22] The observed differences have helped to clarify solvent effects on basic strengths.[11a] Recently observed differences in the behavior of triethylamine and 1,3-diphenylguanidine as reference bases in benzene suggested an explanation why changing from water to another solvent may cause a reduction in the strengths of carboxylic acids relative to the strengths of phenols.[3d]

The differing effects of water and benzene on the relative strengths of the six isomeric phenols discussed in this paper illustrate the need for further studies of potential *reference acids* for nonaqueous media. Chelation in *o*-nitrophenols can reasonably be considered a factor in the discrepancies observed, and it seems very desirable to seek out new acidic indicators in which a strong tendency toward chelation is absent.[23]

Acknowledgment.—The author thanks Maya Paabo for assistance in the early stages of this investigation.

(20) The strengths of the two indicators are indicated in Tables II and III. The equilibrium constant obtained for association of triethylamine with benzoic acid in benzene was 3.76×10^3 using bromophthalein magenta E as the indicator, and $3.7_2 \times 10^3$ using 2,5-dinitrophenol (see ref. 3d).

(21) Possible associations involving carboxylic acids were considered further in section 4.1 of ref. 1. Phenols seem much less prone than carboxylic acids to dimerize or undergo other kinds of self-association: for example, see ref. 7 and E. N. Lassettre and R. G. Dickinson, *J. Am. Chem. Soc.*, **61**, 54 (1939). Hydrogen bonding between molecules of phenol and carboxylic acid does not seem a likely source of error in the range of concentrations used in this work.

(22) For examples see ref. 11*a*, Table 7 and related discussion, and ref. 3c.

(23) R. P. Bell and R. R. Robinson (*Trans. Faraday Soc.*, **57**, 965 (1961)) observed exceptional behavior of 2,4- and 2,5-dinitrophenols in dioxane–water mixtures, as compared with several carboxylic acids. Chelation may be suspected as a factor here, too.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, INDIANA UNIVERSITY, BLOOMINGTON, INDIANA]

The Molecular Structure of *n*-Butyl Chloride and *sec*-Butyl Chloride. I. Rigid Framework[1a]

BY T. UKAJI[1b] AND R. A. BONHAM

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The molecular structures of gaseous *n*-butyl chloride and *sec*-butyl chloride have been investigated by the sector-microphotometer technique of electron diffraction. A measured molecular parameter represents the average value found for that parameter not only in a particular rotational isomer, but also for all rotational isomers present in the gas phase at room temperature. The average bond lengths, defined in terms of the electron diffraction variable $r_g(0)$ and listed in the order mentioned above were found to be: C–H = 1.110 ± 0.005 Å., 1.110 ± 0.005 Å.; C–C = 1.533 ± 0.003 Å., 1.534 ± 0.003 Å.; and C–Cl = 1.780 ± 0.004 Å., 1.781 ± 0.004 Å. Angles calculated from the $r_g(0)$ internuclear distances were: ∠C–C–C = 112.1 ± 0.9°, 111.4 ± 1.0°; ∠C–C–Cl = 110.8 ± 1.0°, 112.4 ± 1.2°; ∠C–C–H = 110.6 ± 2.0°, 110.6 ± 2.0°. Average root mean square amplitudes of vibration were found to be: C–H = 0.078 ± 0.004 Å., 0.078 ± 0.004 Å.; C–C = 0.055 ± 0.002 Å., 0.056 ± 0.003 Å.; C–Cl = 0.059 ± 0.003 Å., 0.059 ± 0.004 Å. The uncertainties quoted above are estimates of the precision of the measurements involved and are determined from approximate standard errors obtained in the least squares fits of the experimental data and estimates of uncertainties in the measurements involved in determining the value of the scattering variable $q = 40/\lambda \sin \theta$. These uncertainties do not reflect possible sources of error in the kinematic scattering theory employed.

The structures of the two molecules reported here are part of a larger study, which it is hoped will encompass as many of the butyl halides as possible. This series of molecules has long been used by physical organic chemists to correlate reaction rates with steric hindrance and various electronic effects.[2] It will be the main purpose of this work to look for these same environmental influences on the ground state structures of the molecules studied. The conclusions drawn from the pre-

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(1) (a) Contribution number 1074 from the Chemical Laboratories of Indiana University. The authors wish to thank the National Science Foundation and the Atomic Energy Commission for their financial support of this work. (b) Department of Chemistry, Faculty of Science. Tokyo University, Tokyo, Japan.

(2) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959.

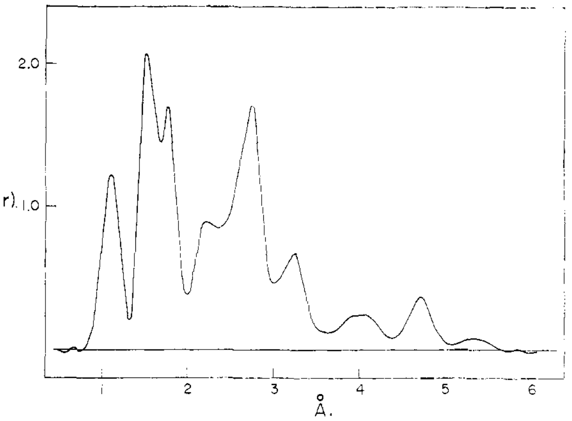

Fig. 1.—Radial distribution curve for *n*-butyl chloride with theoretical data for the small angle scattering with an assumed rotational isomer distribution of 11% TT, 11% GT, 37% TG, 17% GG′ and 24% GG″. (First T or G refers to methyl end of molecule and second to chlorine end. The GG″ form is the most highly coiled of the two GG forms).

vious reaction rate studies may be somewhat ambiguous in this respect since the transition state of the molecule studied may play an important role in determining rate effects. Thus an abnormal rate of reaction for a particular molecule does not necessarily imply an abnormality in the ground state structure.

The method employed to obtain precise measurements of bond lengths and other structural parameters was the sector microphotometer method of electron diffraction. With this technique, it was possible to obtain measurements on the amplitudes of vibration and it was also possible to obtain information on the distribution of internal rotational isomers. The details of rotational analysis are given in a second paper.

Experimental Procedure

Samples of *n*-butyl and *sec*-butyl chloride were obtained from Columbia Chemical Company and purified by gas chromatography. The boiling points and indices of refraction were checked and the samples used appeared to be over 99.5% pure. To avoid the possibility of decomposition, the samples were purified immediately prior to the taking of the electron diffraction photographs. Electron diffraction photographs were obtained with an r^3 sector using the sector electron diffraction camera in Professor L. S. Bartell's laboratory at Iowa State University. Specimen pressures of 20 to 80 mm. with exposure times of 1 to 4 seconds were used at a temperature of 298°K. The beam current was 0.3 μamp. and the accelerating voltage was 40 kv. Four research grade plates at each of two camera distances were obtained for each molecule. The photographic 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 one-quarter millimeter intervals with the aid of a Bausch and Lomb 7 power measuring magnifier. These readings were then punched into IBM cards for the data analysis. The photographic emulsion was calibrated by a procedure due to Bartell and Brockway.[3]

The indices of resolution were found to be 0.90 and 0.95 for the 21.35 cm. camera distance and 1.00 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 a scheme outlined elsewhere.[4a] Bond lengths, vibrational amplitudes and information on hindered rotation were all obtained by analysis of the data using least squares procedures. Corrections to the data for electron-electron scattering, asymmetry of vibration for bonded distances, and Fourier integral termination errors were applied. Corrections to vibrational amplitudes for the failure of the first Born approximation were made by a procedure described elsewhere.[4b] The calculated experimental radial distribution functions made use of experimental data at integral values of $q(q = 40/\lambda \sin \theta)$ over the range $q = 12$ to $q = 100$. An artificial convergence factor e^{-dq^2} was employed where d was chosen so that the experimental value of $M(q)$ at $q = 100$ was reduced to a tenth of its value.

For the purpose of analysis of the data for bond lengths, vibrational amplitudes of bonded distances and the shorter non-bonded distances, not depending on the internal motion of the molecule, a combination of correlation and radial distribution procedures was used. In the correlation procedure the reduced intensity function $M(q)$ was calculated for the region $q = 60$ to $q = 100$ for various theoretical models and comparisons with experiment were made. In the radial distribution technique, the modified radial distribution function $f(r)'$ was obtained by a Fourier transformation of the experimental $M(q)$ function using the Karle non-negative area criterion,[5] the smoothly drawn background function needed to define $M(q)$ was determined.

To simplify the analysis, it was assumed that all C–C bonded distances were equivalent. This assumption was also made for the C–H bonded distances and those bond angles that were independent of the internal motion (*i.e.* ∠ C–C–C and ∠C–C–H) of the molecules. These assumptions mean that the distances reported are average values and deviations in these distances from molecule to molecule would give some indication of the validity of these assumptions. Previous work on the normal hydrocarbons[6] indicates for C–H and C–C bonded and non-bonded distances that the above assumptions were valid within the limits of the experimental precision for the molecules *n*-butane through *n*-heptane.

Theoretical reduced intensity function data were used in the region $q = 0$ to $q = 14$. Various assumptions were made as to the distribution of internal rotational isomers and an analysis of the radial distribution curve for the bonded distances was carried out for each assumed internal rotational configuration. The results of these analyses showed that the distances obtained were independent of the assumptions as to the internal motion of the molecules.

TABLE I

STRUCTURAL PARAMETERS DERIVED FROM RADIAL DISTRIBUTION CURVES AND CALCULATED PRECISIONS

$r_g(0)$, Å.	*n*-Butyl chloride	*sec*-Butyl chloride	Calcd. value
C–H	1.110$_5$ ± 0.005	1.109$_5$ ± 0.005	
C–C	1.533$_6$ ± .003	1.533$_5$ ± .003	
C–Cl	1.780$_0$ ± .004	1.780$_9$ ± .004	
H—H	1.817 ± .04	1.817 ± .04	
C—H	2.188 ± .04	2.187 ± .04	
C—C	2.545 ± .01	2.533 ± .01	
C—Cl	2.731 ± .020	2.758 ± .025	
∠CCH	110.6 ± 2.0°	110.6 ± 2.0°	
∠CCC	112.1 ± 0.9°	111.4 ± 1.0°	
∠CCCl	110.8 ± 1.0°	112.4 ± 1.2°	
l_{ij}, Å.			
C–H	0.078 ± 0.004	0.078 ± 0.003	0.078^a
C–C	.055 ± .002	.056 ± .003	.050^a
C–Cl	.059 ± .003	.059 ± .004	.050^b
C—H	.111 ± .010	.110 ± .010	.11^a
C—C	.076 ± .010	.080 ± .010	.069–0.079^a
C—Cl	.073 ± .020	.075 ± .020	....

^{a} Calculated by Kuchitsu for *n*-butane from force constant data. K. Kuchitsu, *Bull. Chem. Soc. Japan*, **32**, 748 (1959). ^{b} Calculated by Y. Morino, K. Kuchitsu, A. Takahashi and K. Maeda, *J. Chem. Phys.*, **21**, 1927 (1953).

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

(4) (a) R. A. Bonham and L. S. Bartell, *J. Chem. Phys.*, **31**, 702 (1959). (b) R. A. Bonham and T. Ukaji, *ibid.*, **36**, 72 (1962).

(5) I. L. Karle and J. Karle, *ibid.*, **17**, 1052 (1949).

(6) R. A. Bonham, L. S. Bartell and D. A. Kohl, *J. Am. Chem. Soc.*, **81**, 4765 (1959).

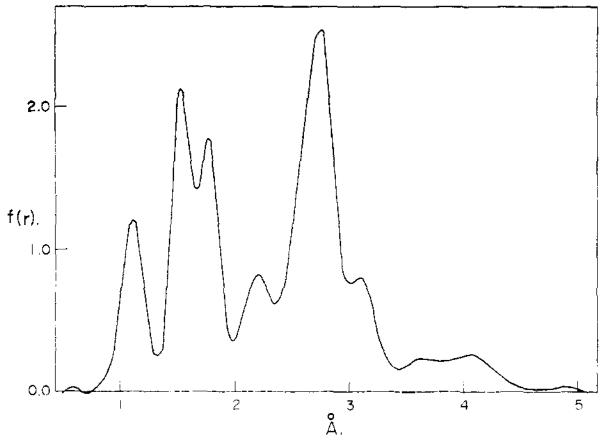

Fig. 2.—Radial distribution curve for *sec*-butyl chloride with theoretical data for the small angle scattering with an assumed rotational isomer distribution of 25% GT, 48% TG and 27% GG. (First T or G refers to methyl–methyl distance and second to methyl–chlorine distance.)

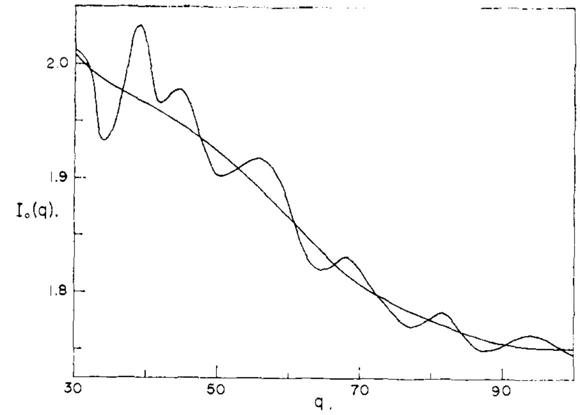

Fig. 3.—Experimental short camera distance intensity curve for *n*-butyl chloride showing the background function (smooth solid line) used in calculating the radial distribution function shown in Fig. 1.

Results

Table I shows a comparison of the final least squares analysis of the radial distribution curves shown in Figs. 1 and 2. The approximate standard deviations of the least squares fits were calculated from equations 12a and 12b of ref. 4a. These equations will tend to underestimate the error in the case of overlapping peaks. These values thus furnish an approximate lower bound on the standard deviation for the least squares analysis of the radial distribution curve. To obtain a total estimate of the precision involved in the various measurements, it is necessary also to include a scale factor error of two parts per thousand. It is somewhat dangerous to interpret the estimates of precision as estimates of the absolute error in measuring a bond length or vibrational amplitude since there are several possible sources of error from use of an approximate theory for the scattering equations which have not yet been completely analyzed.

In Figs. 3 and 4, the experimental intensity curves are shown with the background function determined by the Karles' procedure. The data shown in these curves were obtained by using a 10.66 cm. camera distance. Data obtained from

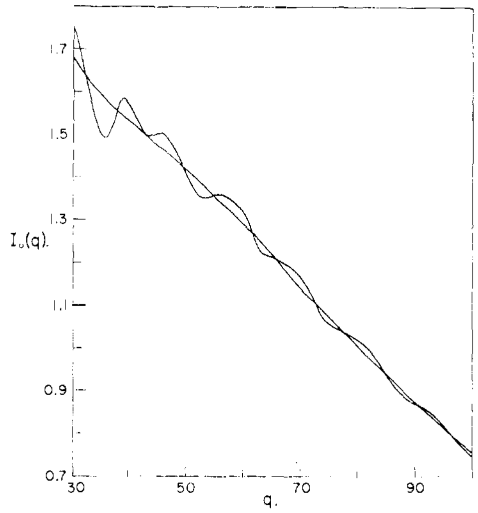

Fig. 4.—Experimental short camera distance intensity curve for *sec*-butyl chloride showing the background function (smooth solid line) used in calculating the radial distribution function shown in Fig. 2.

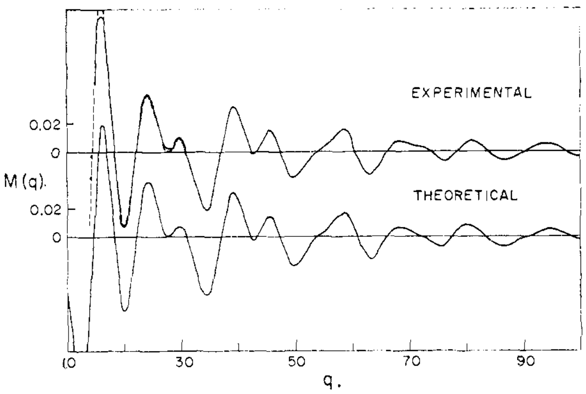

Fig. 5.—Reduced molecular intensity curves for *n*-butyl chloride. The solid line curves have been corrected for the effect of electron–electron scattering and the dotted line represents the uncorrected reduced intensity curve.

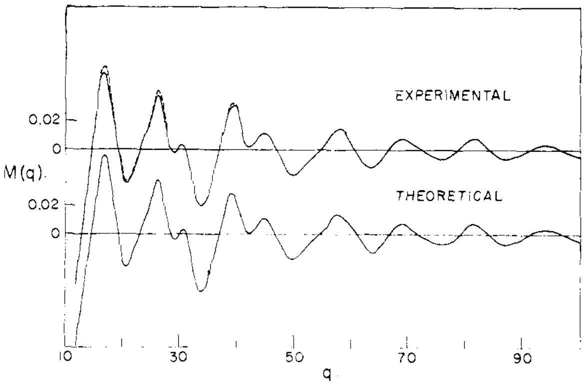

Fig. 6.—Reduced molecular intensity curves for *sec*-butyl chloride. The solid line curves have been corrected for the effect of electron–electron scattering and the dotted line represents the uncorrected reduced intensity curve.

TABLE II

OTHER STUDIES OF MOLECULES WITH SIMILAR PARAMETERS

r_{ij}, Å.	*n*-Butane E.d.[a]	*n*-Pentane E.d.[a]	Methyl chloride E.d.[b]	Ethyl chloride M.w[c]	Ethyl chloride M.w.[d]	*n*-Propyl chloride E.d.[e]
C-H	1.108 ± 0.004	1.118 ± 0.004	1.11 ± 0.01	1.113	1.110	1.09
C-C	1.533 ± .002	1.533 ± .003	....	....	1.550_8	1.535 ± 0.002
C-Cl	....	....	1.784 ± 0.003	1.781	1.777_0	1.775 ± 0.002
C—H	2.183 ± .005	2.188 ± .004	....	...	....	....
C—C	2.547 ± .005	2.552 ± .003	....	...	....	....
C—Cl	....	....	....	...	....	2.73
∠CCC	112.4 ± .3°	112.9 ± .2°	....	...	....	109.5 ± 2.5°
∠CCCl	....	....	....	...	110.5°	111 ± 2°
l_{ij}, Å.						
C-H	0.078 ± 0.004	0.083 ± 0.004	0.089 ± 0.010	...	....	0.067
C-C	.056 ± .003	$.057_5$ ± $.002_5$	....	...	....	.036
C-Cl	....	....	0.060 ± 0.004	...	....	.051
C—H	.106 ± .006	.116 ± .005	....	...	....	...
C—C	.079 ± .005	.080 ± $.003_5$	....	...	....	...

[a] Ref. 6. [b] L. S. Bartell and L. O. Brockway, *J. Chem. Phys.*, **23**, 1860 (1955). [c] S. L. Miller, L. C. Aamodt, G. Dousmouis and C. H. Townes, *ibid.*, **20**, 1112 (1952). [d] R. S. Wagner and B. P. Daily, *ibid.*, **23**, 1355 (1955). [e] Y. Morino and K. Kuchitsu, *ibid.*, **28**, 175 (1958).

a 21.35 cm. camera distance were also used in the analysis and the data from the two different distances were spliced together at the midpoint of their mutual overlap region.

In Figs. 5 and 6, a comparison of the theoretical and experimental reduced intensity functions is presented. The differences between the dotted and solid lines on the experimental $M(q)$ curves shows the magnitude of the electron–electron scattering correction.

Table II presents a comparison of data for various pertinent angles and distances from other molecules with the values found in this investigation. The values for the bonded distances seem to be in good agreement with those of previous investigations on similar types of systems. The C–H distances are in good agreement with those found in *n*-butane and the C–C distances agree very well with those found in the normal hydrocarbons by electron diffraction. The C–Cl distances seem to agree quite well with both the electron diffraction and microwave values for similar types of molecules. In fact, the standard deviation associated with the averaging of all the results in Tables I and II is only ±0.0024. The average value 1.779_5 for the C–Cl distances might well be considered as the normal value when Cl is bonded to hydrocarbon systems with no abnormal steric influences.

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