August, 1981] © 1981 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 54, 2435—2438 (1981) 2435

Molecular Structure of Bromotrichloromethane as Determined by Gas Electron Diffraction

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(Received December 18, 1980)

The molecular structure of $CBrCl_3$ has been determined by gas electron diffraction to be as follows: r_g(C–Cl)$=1.765_4(1_7)$ Å, r_g(C–Br)$=1.944(4)$ Å, and $\angle$ClCCl$=109.7_4(1_3)$°.† The mean amplitudes have been fixed at the calculated values in the data analysis. The result has been compared with the structures of related halomethanes.

The molecular structures of halomethanes have been investigated extensively,[1] but modern structural data are relatively few for halomethanes containing different halogen atoms.[2] Recently, precise structures of HCBrClF,[3] CF_3Cl,[4] CF_3Br, and CF_3I[4,5] have been reported. The C–F bond lengths of CF_3X molecules decrease with increasing electronegativity of atom X(X=H, I, Br, Cl, and F),[4] while the bond angles show only a slight and unsystematic change in value from H to F.[5] A more distinct change in value of bond angles is found for CCl_3X molecules (X=H, Cl, and F).[2] The molecular structure of bromotrichloromethane was determined only by the visual method of gas electron diffraction;[6,7] no accurate geometry of $CBrCl_3$ is available. The present study has been undertaken to supplement the structural data of halomethanes and to compare the structure of $CBrCl_3$ with the geometries of related halomethanes.

Experimental

A sample with the stated purity of at least 99% was obtained from Nakarai Chemical Co., Ltd. and used without further purification. Diffraction patterns were recorded on Kodak electron image plates using an electron diffraction unit[8] equipped with an r^3-sector at two camera distances, 109.3 and 244.3 mm. Experimental conditions were as follows: accelerating voltage, about 39 kV; sample pressure, 20 Torr; vacuum pressure during experiment, $(5-9)\times10^{-5}$ Torr; nozzle temperature, about 18 °C; beam currents, 0.15 and 0.23 μA; exposure times, about 3 and 1 min for the short and long camera distances respectively. The electron wave length was determined from the diffraction patterns of carbon disulfide taken in the same sequence of exposures. The drift of the accelerating voltage was monitored throughout the experiments by measuring the voltage drop of the standard resistance in a high-voltage source.[9] The drift of the wave length during each experimental sequence was confirmed to be less than 0.01%. The number of plates used for data analysis was four and five for the short and long camera distances respectively.

Calculation of Mean Amplitudes

A radial distribution curve obtained from long camera data is shown in Fig. 1. The overlap of C–Cl and C–Br peaks and that of Cl···Cl and Cl···Br peaks indicate difficulty in the precise determination of experimental mean amplitudes. In the data analysis, the mean amplitudes were fixed at the calculated values. Quadratic force constants are needed for the calculation of the mean amplitudes. Zietlow *et al.* reported a quadratic force field for $CBrCl_3$ based on the fundamental frequencies observed for the liquid phase.[10] Recently Clark *et al.*[11] reported the fundamental frequencies for the gas phase which are significantly different from those for the liquid. The force field given by Zietlow

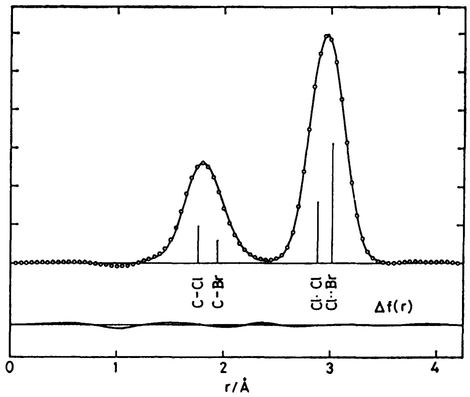

Fig. 1. Experimental (open circles) and theoretical (solid curve) radial distribution curves for $CBrCl_3$; $\Delta f(r)=f(r)^{obsd}-f(r)^{calcd}$. A damping factor, $\exp(-0.0075\,s^2)$, was used.

TABLE 1. F_S-MATRIX ELEMENTS OF $CBrCl_3$[a]
(in md/Å units)

		Zietlow *et al.*[b]	Present
A_1 species	F_{11}	4.073	4.073
	F_{12}	0.182	0.166
	F_{13}	0.654	0.600
	F_{22}	0.374	0.376
	F_{23}	−0.379	−0.370
	F_{33}	2.898	2.898
E species	F_{44}	3.150	3.198
	F_{45}	−0.360	−0.343
	F_{46}	0.361	0.355
	F_{55}	0.344	0.345
	F_{56}	−0.043	−0.040
	F_{66}	0.377	0.349

a) The force constants are expressed in the symmetry coordinates defined in Ref. 12, except for the neglect of deviations from tetrahedral bond angles. b) Transformed from the internal coordinate force constants gven in Ref. 10.

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† Throughout this paper 1 Å$=10^{-10}$ m and 1 Torr≈133.3 Pa are used.

TABLE 2. CALCULATION OF THE MEAN AMPLITUDES, THE STRETCHINGS DUE TO PERPENDICULAR THERMAL VIBRATIONS, AND THE CENTRIFUGAL STRETCHINGS FOR $CBrCl_3$[a] (in 10^{-4} Å)

	C–Cl	C–Br	Cl⋯Cl	Cl⋯Br
l	517	530	689	695
$(\langle\Delta x^2\rangle+\langle\Delta y^2\rangle)/2r$	30	20	17	9
δr_{cent}	3	6	5	8

a) Calculated at 291 K.

et al. was then modified in the present study to reproduce the gas-phase frequencies. The force constants thus obtained in the symmetry coordinates are listed in Table 1 together with Zietlow's values rewritten in the symmetry coordinates. Although there is some arbitrariness in the choice of the force field, the above force constants are sufficient for our purpose, since the mean amplitudes are not sensitive to force constants chosen as long as they reproduce the vibrational frequencies correctly.[13] In Table 2 are listed the calculated values of the mean amplitudes, along with the stretchings due to the perpendicular thermal vibration and the centrifugal stretchings δr_{cent} to be used for shrinkage correction.[14,15]

Data Analysis

Optical densities measured at an interval of 1/3 mm on each photographic plate were converted to intensities.[9] The intensities were corrected for the imperfection of the sector shape and leveled by the theoretical background. Reduced molecular scattering intensities, $sM(s)$, were obtained by drawing a smooth background through the leveled intensities, then the background was revised by applying the non-negativity criterion to radial distribution curves calculated from $sM(s)$ and the drawing procedure was repeated. Data from the two camera distances covered the s-ranges of 2.8 and 17.4 Å^{-1} and 6.0 and 37.4 Å^{-1}. The elastic and inelastic scattering factors were taken from the literature.[16] The asymmetry parameters, κ, for C–Cl and C–Br were estimated from the formula[17]

$$\kappa \simeq \frac{a}{6}l^4,$$

where the Morse parameter, a, was assumed to be 2 Å^{-1}. The asymmetry parameters for the non-bonded atom pairs were assumed to be zero. The parameters adjusted by the least-squares analysis of $sM(s)$ constrained to C_{3v} symmetry were r_a(C–Cl), r_a(C–Br), ∠ClCBr, and the index of resolution.[18] A conventional diagonal weight matrix was used.[9]

The observed values of $sM(s)$ and the best fit curve for one plate from each camera distance are shown in Fig. 2.[19] The parameter values obtained from each camera-distance data are listed in Table 3; these data converted to the thermal average structure are listed in Table 4 together with the weighted averages. The limits of error for the parameter values were estimated from 2.6 times the larger of the random standard deviations, σ_1 and σ_2, and the systematic errors. The errors in the scale factor were estimated to be 0.05% and 0.06% for the short and long camera distance data respectively. The systematic errors originating from the uncertainties of the anharmonicity parameters and those of correction values for the sector shape were also taken into consideration.[9] Other details of the analytical procedures are described elsewhere.[9] The experimental errors are smaller for the long distance data than for the short distance data. The agreement between the two data is satisfactory. The weighted average is given as the final result of the present work.

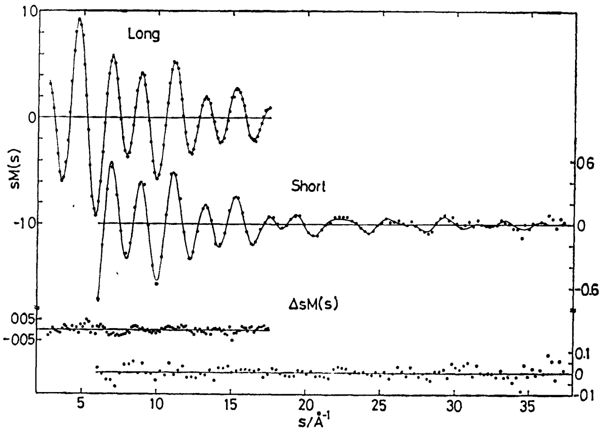

Fig. 2. Experimental (dots) and theoretical (solid curve) molecular intensities for $CBrCl_3$; $\Delta sM(s)=sM(s)^{\mathrm{obsd}}-sM(s)^{\mathrm{calcd}}$.

TABLE 3. RESULTS OF THE LEAST-SQUARES ANALYSIS[a] (in Å and degree units)

		Average	σ_1[b]	σ_2[b]
Short	r_a(C–Cl)	1.7638	0.0010	0.0005
	r_a(C–Br)	1.9442	0.0032	0.0025
	∠ClCBr[c]	109.27	0.10	0.09
	R[d]	0.19_8		
Long	r_a(C–Cl)	1.7639	0.0005	0.0006
	r_a(C–Br)	1.9423	0.0015	0.0016
	∠ClCBr[c]	109.18	0.05	0.04
	R[d]	0.05_4		

a) Indices of resolution are 0.86—0.88 and 0.92—0.97 for the short and long camera distance data, respectively. b) For the definitions of σ_1 and σ_2, see Ref. 20. c) Defined in the r_α structure. d) $R=\{\sum_i w_i(\Delta sM(s)_i)^2/\sum_i w_i(sM(s)_i^{\mathrm{obsd}})^2\}^{1/2}$ where $\Delta sM(s)_i=sM(s)_i^{\mathrm{obsd}}-sM(s)_i^{\mathrm{calcd}}$.

TABLE 4. MOLECULAR PARAMETERS OF BROMOTRICHLOROMETHANE[a] (in Å and degree units)

Parameter	Short	Long	Weighted average
r_g(C–Cl)	$1.765_3(3_0)$	$1.765_4(2_0)$	$1.765_4(1_7)$
r_g(C–Br)	$1.945_6(8_4)$	$1.943_7(4_5)$	1.944(4)
∠ClCBr[b]	$109.2_7(2_7)$	$109.1_8(1_4)$	$109.2_0(1_3)$
∠ClCCl[b]			$109.7_4(1_3)$

a) The numbers in parentheses represent the estimated limits of error attached to the last significant digits. b) Bond angles defined in the r_α structure.

Discussion

The bond lengths of $CBrCl_3$ are compared with those of tetrahalomethanes in Fig. 3. Only modern structural data are collected here. The data for CF_3X(X=Cl, Br, I) and CF_4 are taken from Typke *et al.*[4] and Fink *et al.*'s[21] papers respectively and those for $CFCl_3$ from the Landolt-Börnstein table.[2] The structures of CCl_4 and CBr_4 have been determined in our laboratory.[22,23] Carbon-halogen bond lengths, r(C–W), in tetrahalomethanes, CWXYZ, are plotted against the sums of electronegativity values[††] for the other halogen atoms, X, Y, and Z. In general, the carbon-halogen bond length decreases with an increase in the sum of the electronegativity values. This trend is in accordance with a prediction given by the valence-shell electron-pair repulsion (VSEPR) theory.[25] According to this theory, replacement of neighboring atoms by more electronegative ones shortens the bond length of interest. However, the trend of change in bond lengths is reversed to that expected by the VSEPR theory for CBr_4 and $CBrCl_3$ and for $CBrCl_3$ and CCl_4. This shows that factors governing the geometry of halomethanes are not so simple as those for most inorganic molecules.

The values of ∠ClCCl for related halomethanes are compared in Table 5. As stated before, the bond angle of the CCl_3 group changes considerably with substituents in contrast with that of the CF_3 group. It is noted that the ClCCl angle of $CBrCl_3$ is slightly larger than the tetrahedral angle. This is also inconsistent with the VSEPR theory.

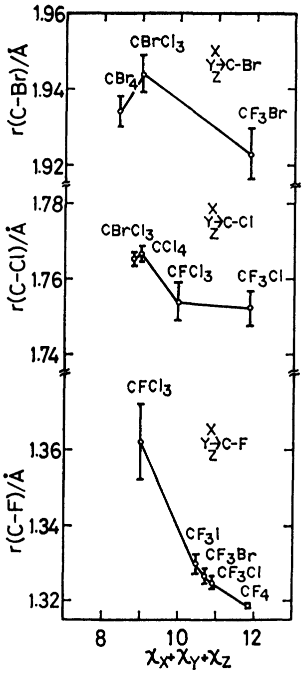

Fig. 3. Plots of carbon-halogen bond lengths of tetrahalomethanes *versus* the sums of electronegativities of adjacent halogen atoms.

Table 5. Comparison of ∠ClCCl (in degrees)

	Obsd	Calcd[a)]	Calcd[b)]
CCl_4	109.5	109.5	109.5
$CBrCl_3$	$109.7_4(1_3)$	110.4	110.5
$CFCl_3$	111(1)[c)]	111.4	111.5
$CHCl_3$	111.3(2)[c)]	112.0	112.0

a) Molecular mechanics calculation given in Ref. 26 b) Given by molecular mechanics calculation with experimental bond lengths. c) Taken from Ref. 2.

Dashevskii calculated the bond angles of halomethanes by means of molecular mechanics.[26] As shown in Table 5, column 3, his results are in fair agreement with the experimental values. In his calculation, the nonbonded atom potential of a 6-exp type was adopted and the same elastic constant was used for all the bond angles, while the bond lengths were fixed at the following values: C–H 1.10, C–F 1.34, C–Cl 1.77 and C–Br 1.93 Å. The experimental bond lengths differ from the assumed values by as much as 0.02 Å and accordingly a different choice of bond lengths may change the result. Thus, the bond angles were recalculated with the experimental bond lengths, but the change is small, as is shown in Table 5, column 4. The agreement between calculation and experiment suggests that the steric effect is an important factor governing the bond angles of trichloromethanes.

The authors wish to thank Dr. Koichi Tamagawa for his helpful discussions. The numerical computations were carried out on a HITAC M180 of the Hokkaido University Computing Center.

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