

# Conformational Analysis. I. The Molecular Structure, Torsional Oscillations, and Conformational Equilibria of Gaseous 1,2,3-Tribromopropane as Determined by Electron Diffraction and Compared with Semiempirical Calculations

REIDAR STØLEVIK

Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

Gaseous 1,2,3-tribromopropane has been studied by electron diffraction at a (nozzle) temperature of 88°C. Three different pairs of enantiomeric conformations were detected: 82 % (2) of GG(ag) + GG(ga), 8 % (4) of GA(gg) + AG(gg), and 10 % (4) of AG(ga) + GA(ag); see Fig. 1. The following values for distances ( $r_a$ ) and angles ( $\angle_\alpha$ ) are appropriate for the structure of the most abundant conformer:

C—H = 1.132(18) Å, C—C = 1.534(12) Å,  
 C—Br = 1.948(6) Å,  $\angle_{CCC} = 117.4^\circ(1.4)$ ,  
 $\angle_{C_2CX} = 110.4^\circ(0.8)$ ,  $\angle_{CC_2X} = 110.5^\circ(0.6)$ ,  
 $\angle_{C_2CH} = 110.8^\circ(2.0)$ ,  $\angle_{CC_2H} = 109.1^\circ(2.0)$ .

Results are presented with error limits ( $2\sigma$ ). Non-bonded distances were computed as dependent quantities, restricted under the constraints of geometrically consistent  $r_\alpha$  parameters.

The torsional angles of the conformers have been determined and their values are significantly different from exact staggered values, in agreement with semiempirical calculations.

Torsional force constants and frequencies, 45  $\text{cm}^{-1}(10)$  and 86  $\text{cm}^{-1}(10)$ , corresponding to torsional modes in the most abundant conformer, were determined by combining information from electron diffraction and vibrational spectroscopy. The observed spectroscopic frequencies (97  $\text{cm}^{-1}$  and 107  $\text{cm}^{-1}$ ) do not agree with the "electron-diffraction" values. Torsional force constants compatible with the spectroscopic frequencies lead to mean amplitudes of vibration significantly smaller than those observed.

Semiempirical calculations of conformational energies, geometries, barriers, and torsional force constants have been carried out, and some shortcomings of the present semiempirical force field are pointed out.

## I. INTRODUCTION

The present work is one of several in a series of electron-diffraction studies. The investigations are concerned with substituted propanes and related molecules in an attempt to understand and quantitatively describe the conformational equilibria in these molecules in the gas phase.

1,2,3-Trisubstituted propanes represent an interesting and complex problem of structural chemistry. Simultaneous rotation about the two C—C bonds can occur, therefore the number of staggered conformers is nine. The numbering and system of naming for conformers of 1,2,3-tribromopropane (TBP) adopted here are presented in Fig. 1. Unfortunately there is no general agreement about the nomenclature in this type of compounds.

The system of naming uses four letters: Capital letters, A or G, indicate whether the X atom of a  $-\text{CH}_2\text{X}$  group is *anti* or *gauche* to the  $\text{C}_1\text{C}_2\text{C}_3$  framework. Small letters, a or g, indicate whether the X atom of a  $-\text{CH}_2\text{X}$  group is *anti* or *gauche* to the central halogen atom ( $\text{X}_2$ ). The four letters are then combined in the following way: GA(ag), for example, means that  $\text{X}_1$  is *gauche*, while  $\text{X}_3$  is *anti* to the  $\text{C}_1\text{C}_2\text{C}_3$  framework, further  $\text{X}_1$  is *anti* and  $\text{X}_3$  is *gauche* to the central halogen atom.

GG(ag) and GG(ga) are non-superimposable mirror images of each other (enantiomers), and the present system of naming can distinguish

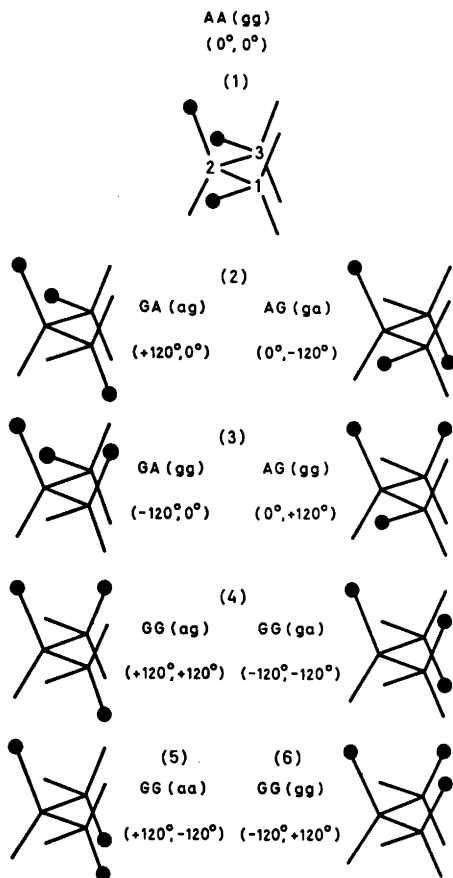


Fig. 1. The numbering and names of staggered conformers in 1,2,3-tribromopropane.

between them. If the numbering  $C_1-C_2-C_3$  is changed to  $C_3-C_2-C_1$ , the enantiomers will have their names exchanged.

Enantiomers cannot be distinguished by electron diffraction, therefore whenever possible, such pairs will be mentioned by a number only, as indicated in Fig. 1. For example, the conformers GG(ag) and GG(ga) may be referred to as conformer (4) (Fig. 2).

## II. CALCULATION OF CONFORMATIONAL ENERGIES, GEOMETRIES, BARRIERS, AND TORSIONAL FORCE CONSTANTS

The method of classical mechanics was used. The method is basically that introduced by Westheimer, as subsequently modified by

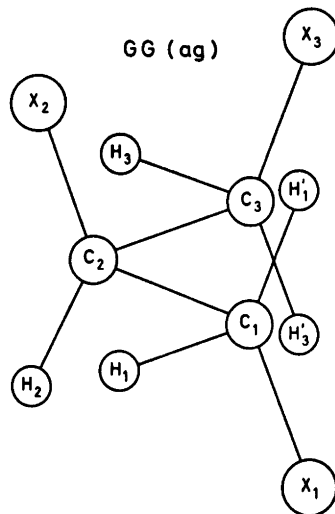


Fig. 2. Numbering of atoms in the conformer GG(ag).

Hendrickson and Wiberg, and widely used by others. Energy parameters were taken from the paper<sup>1</sup> by Abraham and Parry, and references to the original works are found therein.

The energy of a given conformer was calculated from eqn. 1 adjusting the geometry for minimum energy. The computer program that performs all the calculations was written by S. Rustad in FORTRAN.<sup>2</sup>

The energy minimum was in most cases found by a combination of different methods. The method of *steepest descent* was first used, and then close to the minimum *Newton-Raphsons* method was applied. In some cases, only one of the methods was used.

Details about the program will be presented in a forthcoming paper, based upon the thesis of S. Rustad.<sup>2</sup>

$$E = E_r + E_\theta + E_\phi + E_R \quad (1)$$

$E_r = \frac{1}{2} \sum F_r (r - r_0)^2$ ; strain in bond distances.  $r$  represents a bond distance and  $r_0$  the "normal" value of  $r$ .<sup>3</sup>

$F_r$  is the force constant of that bond.

$E_\theta = \frac{1}{2} \sum F_\theta (\theta - \theta_0)^2$ ; strain in bond angles.

$\theta$  represents a bond angle and  $\theta_0$  the "normal" value of  $\theta$ .

$F_\theta$  is the force constant of that angle.

$E_\phi = \frac{1}{2} V_0 \sum \{1 + \cos[3(\phi - \phi_0)]\}$ ; torsional strain.  $\phi$  represents a torsional angle and  $V_0$  is the

Table 1. Calculated conformational energy and geometry of staggered conformers in 1,2,3-tribromopropane.

Parameter (normal value)	GG(ag)	AG(gg)	AG(ga)	AA(gg)	GG(aa)	GG(gg)
C-H(1.094Å)	1.094	1.095	1.094	1.095	1.094	1.095
C-C(1.513Å)	1.528	1.526	1.525	1.525	1.529	1.533
C-X(1.935Å)	1.945	1.945	1.943	1.946	1.941	1.947
$\angle$ CCC(110.0°)	113.6	111.9	111.4	109.7	114.0	115.1
$\angle$ C <sub>2</sub> C <sub>1</sub> X(109.47°)	111.9	111.6	111.0	111.1	112.7	115.0
$\angle$ C <sub>1</sub> C <sub>2</sub> X(109.47°)	110.5	110.8	109.3	109.7	108.9	112.1
$\angle$ C <sub>2</sub> C <sub>1</sub> H(109.47°)	109.8	109.8	110.0	109.9	109.7	109.0
$\angle$ C <sub>1</sub> C <sub>2</sub> H(109.47°)	107.8	109.2	109.3	108.4	105.5	106.6
$\angle$ $\phi_{1-2}(\phi_0)^a$	+117.3	+18.1	+13.0	+11.5	+101.0	-107.1
$\angle$ $\phi_{2-3}(\phi_0)^a$	+122.8	+125.2	-111.2	-11.5	-101.0	+107.1
Energy (kcal/mol)						
<i>E</i> (bonded)	1.16	1.32	0.80	0.85	2.44	4.21
<i>E</i> (van der Waals)	1.09	0.96	0.75	1.17	1.10	2.20
<i>E</i> (polar, X...H)	-6.59	-6.04	-6.29	-5.79	-6.31	-5.68
<i>E</i> (polar, X...X)	4.84	4.93	4.61	4.84	4.77	5.67
<i>E</i> (total)	0.50	1.17	-0.12	1.07	2.01	6.39
<i>E</i> (total) - <i>E</i> [AG(ga)]	0.62	1.29	0	1.19	2.13	6.51

<sup>a</sup>  $\phi_0 = 60^\circ$ , see *E* $\phi$  in eqn. (1), sect. II.

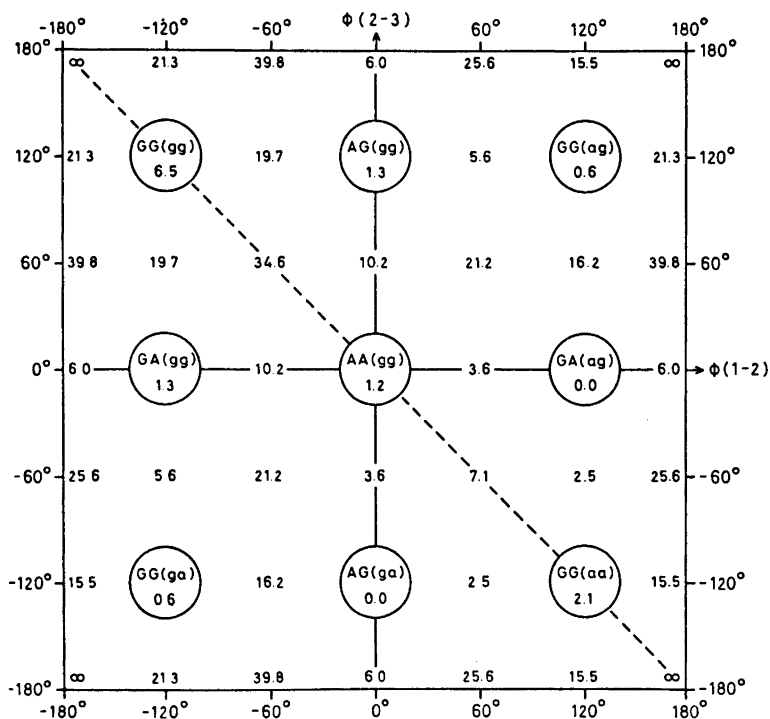


Fig. 3. Potential energy map for 1,2,3-tribromopropane. The numbers within the square are energy values corresponding to a conformation having most structural parameters minimized; see also text. The lowest energy value, for AG(ga) or GA(ag), is arbitrarily set equal to zero.  $\phi_{1-2}$  and  $\phi_{2-3}$  are torsion angles; see Fig. 1.

intrinsic torsional barrier,<sup>1</sup>  $\phi_0 = 60^\circ$ .

$$E_R = \sum (a \exp(-bR) - c/R^6 + d/R)$$

$R$  represents a distance between two atoms *not bonded to the same carbon atom*: The first two terms in the summation of  $E_R$  represents repulsive and attractive van der Waals interactions, respectively, and the third term gives the electrostatic interaction of the polar substituents.

The choice of force constants and "normal" values<sup>3</sup> is subject to a certain arbitrariness. The force constants actually used are those given in Table 2, and values for  $r_0$  and  $\theta_0$  are shown in Table 1. The parameter  $V_0 = 2.65$  kcal/mol and values for  $a$ ,  $b$ ,  $c$ , and  $d$  were taken from the work of Abraham and Parry.<sup>1</sup>

The zero-point vibrational energy is not included in the energy expression.

In minimizing the energy, the geometry was constrained in the same way as described in sect. V-A in order to keep the number of variables small.

The results of calculations for staggered conformations are given in Table 1, but the values demand a few comments. Firstly, the experimental finding (Table 9) that the conformer GG(ag) is more stable than AG(ga), does not follow from the energy values in Table 1. Secondly, the difference in energy between AG(gg) and AG(ga) is probably not as large as calculated (see sect. VII).

The force field allows the CCC angle to open up, but not as much as demanded by the experimental value of  $117.4^\circ$ .

A map of energies, including staggered and eclipsed conformations, is presented in Fig. 3. Whenever a  $\phi$ -value is close to  $0^\circ$  or  $\pm 120^\circ$ , that parameter has been refined. The energy values for some of the conformers are thus shown in positions which are not exactly corresponding to the  $\phi$  angles obtained. Torsional barriers between conformers might be estimated from this map.

Each value on the potential energy surface corresponds to a conformation having all structural parameters minimized, except for one or two torsion angles being kept at constant values.

If torsional angles alone are used as variables, then the calculated quantities are different from those given here.

Valence torsional force constants were calculated according to their definitions:

$$F_\phi(1-2) = \partial^2 E / \partial \phi_{1-2}^2, \quad F_\phi(2-3) = \partial^2 E / \partial \phi_{2-3}^2, \\ F_\phi(1-2; 2-3) = \partial^2 E / \partial \phi_{1-2} \partial \phi_{2-3}.$$

The derivatives were numerically computed at the minimum of potential energy, and results are given in mdyne Å (rad)<sup>-2</sup>:

Conformer:	GG(ag)	GA(gg)	AG(ga)	AA(gg)
$F_\phi(1-2)$ :	0.165	0.204	0.140	0.154
$F_\phi(2-3)$ :	0.233	0.144	0.183	0.154
$F_\phi(1-2; 2-3)$ :	-0.041	-0.016	-0.022	-0.011

The agreement with torsional force constants determined from the electron diffraction data is quite good for  $F_\phi(1-2)$ , and moderate for  $F_\phi(2-3)$ ; the interaction constant being too small for experimental determination.

Interaction force constants between a torsional angle and other internal coordinates are not included in the valence force field applied in the present work. However, such interaction constants were also calculated with the energy program. All such quantities turned out to be very small.

Anharmonicity is expected in the torsional part of the force field, and will certainly lead to errors in the determination of torsional force constants, obtained from the electron diffraction data, since the vibrational quantities have been calculated using an harmonic force field. No attempt was made to establish anharmonic corrections from the experimental data. But it is possible to get some ideas about the degree of anharmonicity from the energy curves in Fig. 4.

Let us consider the energy minimum corresponding to the conformer GG(ag). The deviations from parabolic behaviour are negligible, near minimum, when  $\phi_{2-3}$  is varied, while variation of  $\phi_{1-2}$  leads to an asymmetric change in the energy. The barrier between GG(ag) and GA(ag) is seen to be much higher than the one between GG(ag) and AG(gg), and this leads to asymmetry in the  $\phi_{1-2}$  direction. At higher temperatures the effects of anharmonicity on the observed intensities will be stronger. Anharmonic corrections for the torsional part of the force field must then be considered.

The energy curves in Fig. 4 have been computed by varying  $\phi_{1-2}$  or  $\phi_{2-3}$  while the

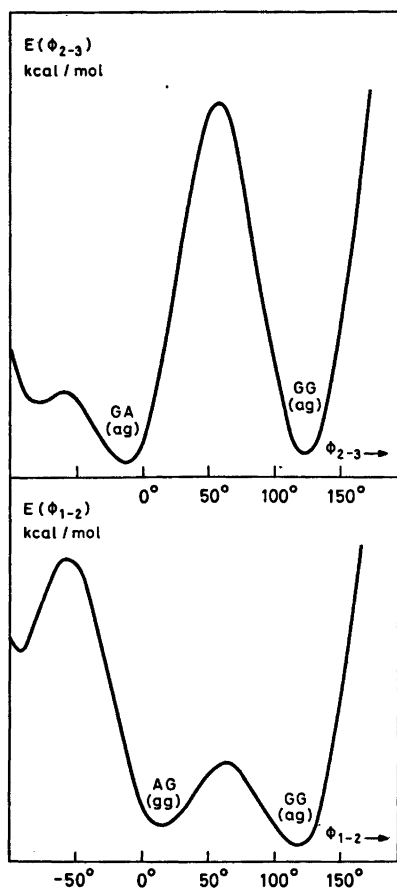


Fig. 4. Energy curves,  $E(\phi_{1-2})$  and  $E(\phi_{2-3})$ , computed by varying the torsional angles  $\phi_{2-3}$  and  $\phi_{1-2}$  separately; the remaining structural parameters were kept at constant values corresponding to GG(ag).

remaining structural parameters were kept at constant values corresponding to GG(ag). The minima, and barriers between them, are therefore better represented by the values in Fig. 3.

The destabilizing effect of parallel (1:3) Br...Br interactions in conformers like GG(aa) and GG(gg) is reproduced by the calculations. However, the minima of these conformers lie at  $(101^\circ, -101^\circ)$  and  $(-107^\circ, 107^\circ)$ , considerably displaced from staggered dihedral angles. Moreover, the CCC angles have been opened up to  $114^\circ$  and  $115^\circ$ , also considerably lowering the conformational energies. There-

fore, the conformer GG(aa) is not much higher in energy than the conformers found to be present in the vapour. Between the conformers GG(aa) and AG(ga), or GA(ag), is a very low barrier [0.4 kcal/mol higher in energy than the minimum of GG(aa)].

The amount of GG(aa) would probably be increased by increases in the temperature, but the very shallow and asymmetrical energy minimum of GG(aa) indicates, that this conformer will be very difficult to detect and determine by electron diffraction, even at a very high temperature.

All the other conformers correspond to well defined minima on the potential surface.

The intention of the author is to use the present force field, without essential changes in parameters, for a series of related compounds. After comparing calculated and experimental results for several molecules, changes in energy parameters are going to be considered.

Some obvious shortcomings of the present force field have already been mentioned. Nevertheless, the results from these calculations are very useful in many ways, despite of the discrepancies pointed out. In particular, the results were valuable in planning the structural analysis. Moreover, the time and efforts demanded are negligible, provided a suitable computer program is at hand. Finally, it must be admitted that some of the experimental findings probably would not have been looked for without the aid of such calculations.

### III. CALCULATION OF VIBRATIONAL QUANTITIES

Valence force constants, except for the torsional part, were taken from the extensive work of Schachtschneider and Snyder on halo-paraffins,<sup>4</sup> and partly from a second work, also by Snyder.<sup>5</sup> It was decided that the degree of transferability was high enough to use their force constants in calculating mean amplitudes and related quantities for TBP. The results of the present investigation strengthen this conclusion.

Certain compromises between force constant values had to be made, and the final values selected for TBP are given in Table 2.

The normal coordinate program described by Gwinn<sup>6</sup> was used in computing vibrational

**Table 2.** Valence force constants for 1,2,3-tribromopropane. The torsional force constants have been defined in the following way: Each fragment of type  $A'-C_1-C_2-A''$  ( $A=H,C,X$ , see Fig. 2) has been assigned an equal torsional force constant. Each fragment of type  $A'-C_1-C_2-A''$  has been assigned an equal force constant but different from those of fragments  $A'-C_1-C_2-A''$ . The total force constant for the torsional coordinate  $\phi_{1-2}$  ( $i=1,3$ ) is thus the sum of *nine* equal contributions. The input to Gwinn's normal coordinate program demands a separate specification for each torsional fragment. Moreover, all interaction force constants have to be multiplied by two if Gwinn's program is used.

Type of force constant	Value in C-CH <sub>2</sub> X	Value in C-CHX-C
<b>Stretch (mdyn Å<sup>-1</sup>)</b>		
C-C	(4.73)	(4.40)
C-H	4.85	4.59
C-X	2.63	2.31
<b>Bend (mdyn Å (rad)<sup>-2</sup>)</b>		
CCC	(0.90)	(0.94)
CCH	0.67	0.66
HCH	0.50	-
CCX	0.91	1.05
HCX	0.69	0.74
<b>Stretch/Stretch (mdyn Å)<sup>-1</sup></b>		
C-X/C-C (C common)	0.350	0.347
C-H/C-H (C common)	-0.007	-
C-C/C-C (C common)	-	0.64
<b>Stretch/Bend (mdyn (rad)<sup>-1</sup>)</b>		
C-X/CCX (C-X common)	0.49	0.42
C-X/HCX (C-X common)	0.26	0.226
C-C/CCX (C-C common)	0.30	0.121
C-C/CCC (C-C common)	(0.35)	(0.225)
C-C/CCH (C-C common)	0.26	0.265
<b>Bend/Bend (mdyn Å (rad)<sup>-2</sup>)</b>		
HCC/CCC (C-C common)	-0.124	-0.136
HCX/HCX (C-X common)	0.050	-
HCC/HCC (C-C common)	-0.026	-
HCC/HCC (C-H common)	-	0.012
HCC/HCX (C-H common)	0.074	0.088
HCC/HCX (C common)	0.029	-
HCC/CCX (C-C common)	-	-0.030
HCX/CCX (C-X common)	-	-0.031
CCX/CCX (C-X common)	-	-0.041
CCC/CCX (C-C common)	-	-0.041
<b>Bend/Bend (C-C common and dihedral angle <i>anti</i> or <i>gauche</i>)</b>		
HCC/CCX	<i>anti</i> 0.022	<i>gauche</i> -0.030
CCC/CCX	0.093	-0.024
HCC/CCC	0.072	-0.058
HCC/HCC	0.106	-0.024
CCX/CCX	-0.001	+0.011
<b>Torsional force constants (mdyn Å (rad)<sup>-2</sup>)</b>		
$F_\phi(1-2)^a = 0.20 \pm 0.05$ , $F_\phi(2-3)^a = 0.41 \pm 0.10$		

Table 3. Vibrational frequencies (cm<sup>-1</sup>) in 1,2,3-tribromopropane.

Approximate mode	Spectroscopic values Ref. 7	Calculated values for conformers			
		(4)	(3)	(2)	(1)
Torsion <sup>a</sup>	97	46	62	55	58
Torsion <sup>a</sup>	107	87	77	98	75
CCX bend	(?) <sup>b</sup>	160	87	117	84
CCX bend	186	167	167	181	198
CCX bend	195	199	292	216	213
CCX bend	308	325	342	342	368
CCC bend	458	471	453	371	413
C-X stretch	562	570	514	571	506
C-X stretch	622	619	590	658	593
C-X stretch	672	696	701	668	722
C-C stretch	954	837	880	849	856
CH <sub>2</sub> rock	849	893	930	940	969
CH <sub>2</sub> rock	867	999	983	999	1001
CH <sub>2</sub> twist	1110	1129	1106	1113	1118
C-C stretch	1071	1142	1145	1141	1126
CH <sub>2</sub> twist	1159	1201	1179	1175	1152
CH def.	1189	1206	1224	1232	1238
CH <sub>2</sub> wag.	1233	1255	1287	1270	1270
CH <sub>2</sub> wag.	1252	1291	1296	1317	1360
CH def.	1329	1362	1371	1377	1368
CH <sub>2</sub> scissor	1414	1421	1430	1430	1416
CH <sub>2</sub> scissor	1429	1425	1435	1434	1421
C-H stretch	2902	2903	2903	2904	2904
C-H stretch	2948	2945	2943	2943	2945
C-H stretch	2970	2946	2944	2944	2946
C-H stretch	3012	3018	3021	3021	3019
C-H stretch	3027	3021	3022	3022	3022

<sup>a</sup> An average torsional force constant  $\overline{F}_\phi = 0.304 \text{ mdyn } \text{\AA} (\text{rad})^{-2} F_\phi(1-2) = F_\phi(2-3) = \overline{F}_\phi$ , was used, and the remaining force field is found in Table 2. For definition of  $F_\phi$  values see text to Table 2.

<sup>b</sup> See Ref. 7.

frequencies. Results for some staggered conformers are presented in Table 3, together with the spectroscopic frequencies observed by Thorbjørnsrud *et al.*<sup>7</sup>

Mean amplitudes of vibration were calculated as described in Ref. 8. In Table 4 are given the  $u$  and  $K$  values of the conformer GG(ag).

Since observed frequencies are available, it is possible to adjust the force constants of Table 2 to fit TBP even better. However, this was not done for several reasons. The aim was to calculate mean amplitudes of vibration to be used in the structure analysis. The force field required for this purpose may be rather approximate. The  $u$  and  $K$  values are quite insensitive to moderate errors in the force field, except for the torsional part of it, which has been adjusted (see sect. V-B).

Moreover, it is important to make use of *typical* force constants as much as possible to test the degree of transferability and usefulness in various situations. The works by Snyder<sup>5</sup> and Schachtschneider<sup>4</sup> are in this respect extremely valuable. Their information, combined with electron-diffraction data, made it possible to determine the torsional force constants for the most abundant conformer of TBP. Several vibrational quantities in a molecule like TBP varies with the torsional force constants. To illustrate this point some of the quantities have been calculated using three different values of the average ( $F_\phi(1-2) = F_\phi(2-3) = \overline{F}_\phi$ ) torsional force constant, and the results are found in Table 5.

Table 4. Mean amplitudes ( $u$ ) and  $K$  values for the conformer GG(ag) of 1,2,3-tribromopropane at 88°C. The conformation was staggered, ( $\phi_{1-2} = \phi_{2-3} = 120^\circ$ ) and the valence force field has been given in Table 2. The numbering of atoms is shown in Fig. 2.

Type of distance	Dist. (Å)	$F_\phi(1-2) = 0.203$ $u$ (Å)	$F_\phi(2-3) = 0.406$ $K$ (Å)	$F_\phi(1-2) = F_\phi(2-3) = 0.304$ $u$ (Å)	$K$ (Å)
C <sub>2</sub> -H <sub>3</sub>	(1.13)	.0791	.0157	.0791	.0156
C <sub>1</sub> -H <sub>1</sub> '	(1.13)	.0780	.0252	.0780	.0222
C <sub>1</sub> -H <sub>1</sub>	(1.13)	.0780	.0249	.0780	.0218
C <sub>3</sub> -H <sub>3</sub> '	(1.13)	.0780	.0213	.0780	.0229
C <sub>3</sub> -H <sub>3</sub>	(1.13)	.0780	.0202	.0780	.0217
C <sub>1</sub> -C <sub>3</sub>	(1.53)	.0512	.0055	.0513	.0053
C <sub>2</sub> -C <sub>3</sub>	(1.53)	.0513	.0051	.0513	.0050
C <sub>2</sub> -X <sub>2</sub>	(1.95)	.0587	.0064	.0587	.0060
C <sub>1</sub> -X <sub>1</sub>	(1.95)	.0554	.0173	.0554	.0134
C <sub>3</sub> -X <sub>3</sub>	(1.95)	.0554	.0135	.0555	.0154
C <sub>3</sub> ...X	(2.83)	.0795	.0094	.0794	.0080
C <sub>2</sub> ...H	(2.23)	.1086	.0177	.1085	.0157
C...C	(2.64)	.0712	.0057	.0712	.0056
C...X <sub>3</sub>	(2.88)	.0768	.0065	.0769	.0059
C...H <sub>3</sub>	(2.11)	.1097	.0112	.1099	.0111
H...X <sub>1</sub>	(2.53)	.1138	.0290	.1134	.0224
H <sub>1</sub> ...H <sub>3</sub> '	(1.79)	.1290	.0349	.1286	.0298
H <sub>1</sub> ...X <sub>2</sub>	(2.43)	.1163	.0113	.1163	.0109
X <sub>1</sub> ...X <sub>2</sub> (a)	(4.61)	.0819	.0034	.0810	.0035
X <sub>2</sub> ...X <sub>3</sub> (g)	(3.57)	.1678	.0057	.1771	.0051
X <sub>1</sub> ...H <sub>2</sub> (g)	(2.95)	.1803	.0120	.1727	.0110
X <sub>2</sub> ...H <sub>1</sub> '(g)	(3.18)	.1701	.0140	.1621	.0121
X <sub>2</sub> ...H <sub>2</sub> (g)	(2.98)	.1692	.0166	.1632	.0139
X <sub>3</sub> ...H <sub>3</sub> (a)	(3.84)	.1067	.0114	.1066	.0108
X <sub>2</sub> ...H <sub>3</sub> (a)	(3.89)	.1061	.0114	.1063	.0115
X <sub>2</sub> ...H <sub>3</sub> (g)	(2.98)	.1615	.0099	.1647	.0107
X <sub>1</sub> ...C <sub>3</sub> (g)	(3.35)	.1648	.0063	.1542	.0057
X <sub>2</sub> ...C <sub>1</sub> (g)	(3.35)	.1486	.0074	.1542	.0071
X <sub>1</sub> ...X <sub>3</sub>	(4.23)	.2788	.0014	.2676	.0014
X <sub>1</sub> ...H <sub>3</sub> '	(2.94)	.2575	.0155	.2494	.0155
X <sub>1</sub> ...H <sub>3</sub>	(4.35)	.1783	.0081	.1756	.0082
X <sub>3</sub> ...H <sub>1</sub> '	(2.94)	.2461	.0186	.2479	.0164
X <sub>3</sub> ...H <sub>1</sub>	(4.35)	.1767	.0105	.1755	.0096

#### IV. EXPERIMENTAL AND DATA REDUCTION

TBP was obtained from Fluka, and the purity of the actual sample used was better than 98 %. Electron-diffraction photographs were made at a nozzle temperature of 88°C in the Oslo apparatus,<sup>9</sup> under conditions summarized below.

Nozzle-to-plate distance, (mm):	480.76	200.76
Electron wavelength (Å):	0.064616	0.064616
Number of plates:	5	5
Range of data, in $s$ (Å <sup>-1</sup> ):	1.375 - 19.875	7.0 - 44.25
Data interval, $\Delta s$ (Å <sup>-1</sup> ):	0.125	0.250
Uncertainty in $s$ -scale:	0.14 %	0.14 %

The electron wavelength was determined by calibration against gold. The data were reduced in the usual way<sup>10</sup> to yield an intensity curve for each plate.

Average curves for each set of distances were formed. A composite curve was then made by connecting the two average curves after scaling. Unfortunately the quality of the 20 cm data were poor, while the 48 cm data were excellent. The 20 cm data were used, with low weight, in some least-squares refinements. However, in the final adjustments the 20 cm data were not included for  $s > 19.875$  Å<sup>-1</sup>, and all intensities were given equal weight.

The final experimental intensity curve is shown in Fig. 5.



Table 5. Vibrational quantities in 1,2,3-tribromopropane at 88°C. The valence force field has been given in Table 2, and the numbering of atoms is shown in Fig. 2.

Torsional force constants			
$F_\phi(1-2) = F_\phi(2-3) = \bar{F}_\phi$ in mdyn Å (rad) <sup>-2</sup>	0.180	0.304	0.405
Torsional frequencies for conformer (4), in cm <sup>-1</sup>			
	37	46	51
	77	87	91
Ratios between vibrational partition functions ( $Q$ ). (1), (2), (3), and (4) refer to Fig. 1			
$Q_{(4)}(0.304)/Q_{(3)}(\bar{F}_\phi)$	0.41	1.02	1.86
$Q_{(4)}(0.304)/Q_{(2)}(\bar{F}_\phi)$	0.48	1.20	2.19
$Q_{(3)}(0.304)/Q_{(1)}(\bar{F}_\phi)$	0.32	0.80	1.45
$u$ Values for the distance $X_1 \cdots X_3$ , in Å			
In conformer (4)	0.325	0.268	0.243
In conformer (3)	0.158	0.149	0.145
In conformer (2)	0.218	0.195	0.186
In conformer (1)	0.144	0.143	0.143
$u$ Values for $X_2 \cdots X_3$ in GG(ag)	0.202	0.177	0.167

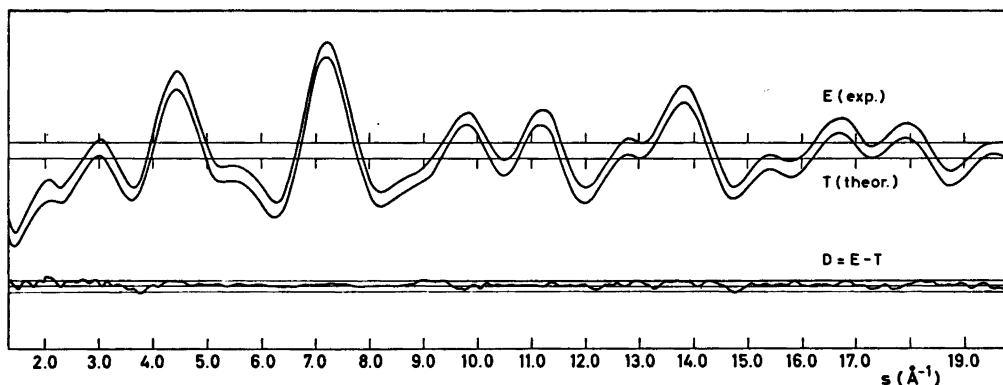


Fig. 5. Curve E shows the experimental intensity, and curve T the theoretical intensity corresponding to the final least-squares parameters. Curve D is the experimental minus the theoretical. The straight lines give the experimental uncertainty ( $\pm 3 \times$  experimental standard deviation).

The intensities have been modified by  $s/f_{\text{Br}}|^2$ . The scattering amplitudes were calculated by the partial wave method<sup>11</sup> using Hartree-Fock atomic potentials.<sup>12</sup>

Contributions to the theoretical intensities from H...H distances, the H atoms bonded to different carbon atoms, were not included.

## V. STRUCTURE ANALYSIS AND REFINEMENTS

The calculated conformational energies for staggered conformers suggest that the amount of conformer (6) is negligible. Conformers (2) and (4) must be expected to be present in detectable amounts. The fact that conformer (4) is the most abundant one, and not conformer (2) as suggested by the calculated energies,

is obvious from the radial distribution (RD) curves in Fig. 6. From the RD curves it also follows that conformer (1) can hardly be present in detectable amounts. Conformer (3) is present, but in small amounts, as also suggested by the results of energy calculations. From the energy calculations, it was concluded that conformer (5) might be present. The contribution to the experimental RD curve would thus be very small.

The conclusion is that conformers (4), (3), and (2) have to be considered in calculating theoretical intensities. Since conformer (4) contributes more than 80 % to the intensities at 88°C, exact structural information about that conformer can be obtained from diffraction data. A limited amount of information can be obtained for the conformers (2) and (3) at 88°C, but the amount of information may be increased by increases in temperature.

*A. Least-squares refinements.* The least-squares program was written by H. M. Seip, and it is a modified version of the one explained in Ref. 10. Several conformers might be included in the refinements with the present version of the program.

The models for the conformers were constructed with the following geometrical assumptions: (1) the plane of the  $H_2C_2X_2$  group is perpendicular to the plane of C atoms and bisect the CCC angle; (2) the two  $C-CH_2X$  groups are equal; (3)  $\angle C_2C_1H_1 = \angle C_2C_1H_1'$  and  $\angle X_1C_1H_1 = \angle X_1C_1H_1'$ , the projection of  $\angle H_1C_1H_1$  on the plane perpendicular to the  $C_1-C_2$  axis is  $120^\circ$ ; (4) all C-H bond lengths are equal; (5) all C-X bond lengths are equal; (6) the conformers have identical structures, except for the C-C torsion angles.

The last assumption is probably the most questionable, and can only be tested if the experiment is carried out at a much higher temperature. The assumptions are partly justified by the results of Table 1, remembering that the conformers AA(gg), GG(aa), and GG(gg) are not present in detectable amounts.

Models were defined in terms of the following average parameters: C-H, C-C, C-X, CCC,  $C_2CX$ ,  $CC_2X$ ,  $C_2CH$ , and  $CC_2H$ . The torsion angles of the conformers were refined, but not all of them independently. Also adjusted were the composition parameters, the relative amounts of the conformers. Non-bonded di-

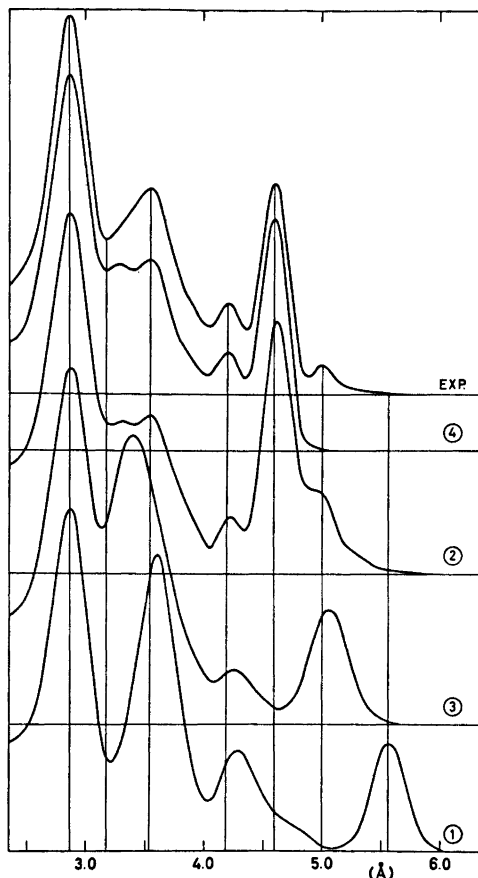


Fig. 6. Theoretical RD curves of four conformers and the final experimental one are shown. The theoretical curves have been labelled in the same way as the conformers in Fig. 1. The artificial damping constant was equal to  $0.0020 \text{ \AA}^2$ .

stances were computed as dependent parameters, restricted under the constraints of geometrically consistent  $r_\alpha$  parameters.<sup>13,14</sup>

Only a limited part of the total experience gained by the investigator himself can reasonably be presented here. In the first part of the structural analysis a large number of refinements were carried out, in which selected combinations of parameters were allowed to vary, while others were held constant at plausible values. It seems practically impossible to report on all these intermediate refinements. At some stages the background had to be corrected,

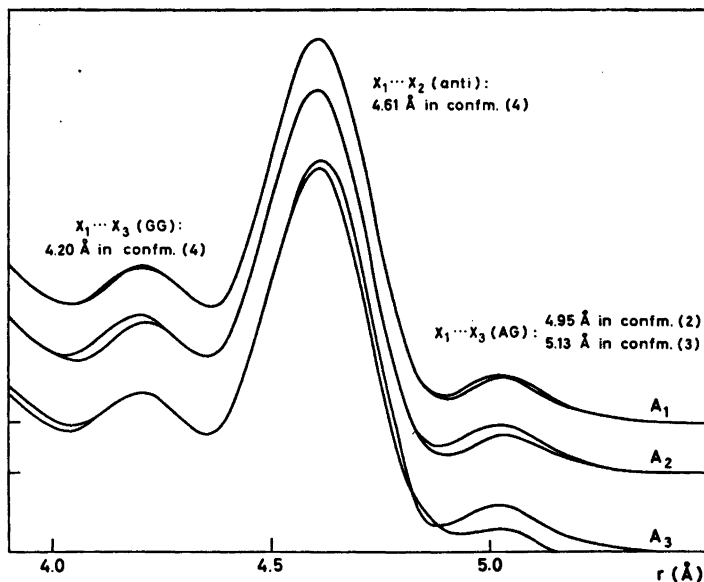


Fig. 7. Three theoretical radial distribution curves are shown together with the final experimental R.D curve. The theoretical curves were calculated under conditions, as follows:

$$\begin{array}{l}
 A_1: \alpha_2 = 10 \%, \alpha_3 = 8 \%, \alpha_4 = 82 \% \\
 A_2: \alpha_2 = 0 \%, \alpha_3 = 12 \%, \alpha_4 = 88 \% \\
 A_3: \alpha_2 = 13 \%, \alpha_3 = 0 \%, \alpha_4 = 87 \%
 \end{array}$$

An artificial damping constant  $0.0020 \text{ \AA}^2$  was used.

and finally the 20 cm data for  $s > 19.875 \text{ \AA}^{-1}$  were excluded because of low quality. However, none of the important conclusions about the structure and composition were changed thereby.

Not all possible parameters could be simultaneously refined. Nevertheless, the combination of all (except for CCH angles) geometry variables, the important  $u$  values for  $X \cdots X$  distances, composition parameter, and a scale factor refined to give convergence and reasonable parameter values. Other combinations, with a reduced number of geometry parameters and a larger number of  $u$  values, also gave convergence.

Least-squares refinements, with the amount of conformer (2) or (3) set equal to zero, were carried out. Radial distribution curves corresponding to these refinements are shown in Fig. 7. It is obvious that a mixture of the conformers (4) and (2) alone does not fit the experimental data very well. Much better fit is obtained with a mixture of (4) and (3), but still the agreement is not quite satisfactory.

The agreement, when all three conformers are included, is seen to be very good.

*B. Determination of torsional force constants.* Mean amplitudes of vibration ( $u$  values) and perpendicular amplitude correction coefficients ( $K$  values) are easily calculated if a reasonable force field is known for the molecule.<sup>8</sup> Torsional force constants were not known for TBP, however, some of the  $u$  values get a considerable contribution from the torsional modes. Therefore, since a reasonable force field is known, except for the torsional force constants, the latter can be adjusted to fit the experimental data. This procedure worked out very well, because some of the  $u$  values, that get large contributions from torsional oscillations, are well determined from the diffraction data. Such  $u$  values are  $u(X_1 \cdots X_3)$  and  $u(X_2 \cdots X_3)$  in conformer GG(ag). Torsional modes alone contribute more than 70% to  $u(X_1 \cdots X_3)$ . Torsional modes also contribute substantially to the  $K$  values.

The following procedure was adopted: First an average torsional force constant ( $\bar{F}_\phi$ ),

$\bar{F}_\phi(1-2) = \bar{F}_\phi(2-3) = \bar{F}_\phi$ , was determined. Parallel and perpendicular amplitudes for several values of  $\bar{F}_\phi$  were calculated and included in the least-squares refinements. The value of  $\bar{F}_\phi$  which lead to minimum in the error sum ( $V'PV$ ) was obtained for  $\bar{F}_\phi = 0.304$  mdyn Å (rad)<sup>-2</sup>.

If the conformer GG(ag) is considered, the force constant  $F_\phi(1-2)$  ought to be less than  $F_\phi(2-3)$ .

Keeping the average value of  $F_\phi(1-2)$  and  $F_\phi(2-3)$  at 0.304 mdyn Å (rad)<sup>-2</sup>, a deeper minimum of  $V'PV$  was obtained with  $F_\phi(1-2) = 0.203$  and  $F_\phi(2-3) = 0.406$  mdyn Å (rad)<sup>-2</sup>.

The interaction constant  $F_\phi(1-2, 2-3)$  could not be experimentally determined. However, the interaction constant has been calculated (sect. III) and the value was  $-0.041$  mdyn Å (rad)<sup>-2</sup>. This value was included in some computations of vibrational quantities. The influence on the vibrational frequencies was small. The effects on  $u$  and  $K$  values were negligible, even with interaction constants given much larger absolute values than 0.041.

It is difficult to estimate uncertainties in the  $F_\phi$  values, but a *minimum* uncertainty might be estimated. The  $u$  values vary approximately as  $u^2 \propto 1/F_\phi$ . Therefore the relative uncertainty in  $F_\phi$  values must be approximately twice the relative uncertainty in the  $u$  values. Only those  $u$  values corresponding to well determined internuclear distances, and having a large derivative with respect to  $F_\phi$ , should be considered.

The final, and most probable, torsional force constants and their estimated error limits are: Conformer GG(ag):

$$F_\phi(1-2) = 0.20 \pm 0.05 \text{ mdyn } \text{Å} \text{ (rad)}^{-2}$$

Conformer GG(ag):

$$F_\phi(2-3) = 0.41 \pm 0.10 \text{ mdyn } \text{Å} \text{ (rad)}^{-2}$$

The error limits need a few comments: Not all combinations of  $F_\phi(1-2)$  and  $F_\phi(2-3)$  values are equally probable. Certain combinations of the extremes of the permissible ranges are very much less likely than others. Combinations being highly probable are found within a radius of approximately 0.03 Å (rad)<sup>-2</sup> from the most probable values. The error limits do not allow for systematic errors within the remaining force field. However, the force constants

F(CCX) and F(CCC) seem to be the only critical ones in this respect, but their values are probably close to the correct ones for TBP (See Table 3).

## VI. FINAL RESULTS

Results from least-squares refinements, and standard deviations ( $\sigma$ ), corrected for correlation in the experimental data,<sup>15</sup> are given. Refinements of intensities from five 48 cm plates separately were also carried out, and the standard deviations ( $\sigma_s$ ) calculated from these individual results are shown too. Usually  $\sigma_s$  is much smaller than  $\sigma$ .

Non-bonded distances were restricted under the geometrical constraint of  $r_\alpha$  parameters,<sup>12,14</sup>

*Table 6.* Bond lengths for 1,2,3-tribromopropane. 0.14 % uncertainty in the wavelength has been included in the  $\sigma$ -values. An experiment with CO<sub>2</sub> gave a correction of +0.1 % in the  $s$ -scale, therefore the bond lengths given are 0.1 % longer than those obtained directly by refinements. Parameter correlation involving bond distances was always less than 0.5 in absolute value.

Bond	$r_a(\text{Å})$	$\sigma$	$\sigma_s$
C-H	1.132	0.009	(0.008)
C-C	1.534	0.006	(0.002)
C-Br	1.948	0.003	(0.001)

*Table 7.* Bond angles for 1,2,3-tribromopropane. The CCH angles could not be refined simultaneously along with the other parameters, and their values were finally determined by trial and error. Parameter correlation:  $\rho(\text{CCC}/\phi_C) = 0.91$ ,  $\rho(\text{CCC}/\phi_A) = -0.75$ ,  $\rho(\text{C}_2\text{CX}/\phi_C) = -0.58$ ,  $\rho(\text{C}_2\text{CX}/\phi_A) = 0.59$ ,  $\rho(\text{CC}_2\text{X}/\phi_C) = 0.64$ ,  $\rho(\text{CC}_2\text{X}/\phi_A) = -0.91$ ,  $\rho(\text{CCC}/\text{C}_2\text{CX}) = -0.62$ ,  $\rho(\text{CCC}/\text{CC}_2\text{X}) = 0.53$ ,  $\rho(\text{C}_2\text{CX}/\text{CC}_2\text{X}) = -0.63$ .

Bonds	$\angle_\alpha^\circ$	$\sigma$	$\sigma_s$
CCC	117.4	0.7	(0.2)
C <sub>2</sub> CX	110.4	0.4	(0.1)
CC <sub>2</sub> X	110.5	0.3	(0.1)
C <sub>2</sub> CH	(110.8)	(1.0)	(-)
CC <sub>2</sub> H	(109.1)	(1.0)	(-)

by including correction terms  $D = r_\alpha - r_a$  ( $D = u^2/r - K$ ) for all distances. Calculated  $u$  and  $K$  values, corresponding to final torsional force constants, are shown in Table 4. Bond lengths,  $r_a$  values,<sup>10</sup> are given in Table 6 and bond angles in Table 7.

Several refinements were carried out in order to determine the torsional angles, not all of them being successful. Finally the angles were restricted under constraints which are shown together with their values. Two parameters,  $\phi_A$  and  $\phi_G$  were adjusted, and their meaning is understood when comparing Fig. 1 with the relations in Table 8. Although only two

Table 8. Torsion angles ( $^\circ$ ) for the conformers of 1,2,3-tribromopropane. Parameter correlation:  $\rho(\phi_G/\phi_A) = -0.84$ .

Conformer	$\phi_{1-2}$	$\phi_{2-3}$
GG(ag)	$120^\circ - \phi_G = 114.7$	$120 + \phi_G = 125.3$
AG(gg)	$\phi_A = 12.2$	$120 + \phi_G = 125.3$
AG(ga)	$\phi_A = 12.2$	$\phi_G - 120 = -114.7$
$\phi_G = 5.3$ ( $\sigma = 1.0$ ) and $\phi_A = 12.2$ ( $\sigma = 3.0$ )		

torsional parameters were adjusted, their values are significantly different from  $0^\circ$ , which implies that the conformers most probably have torsion angles different from exact staggered values. If conformers AG(gg) and AG(ga) were assigned torsion angles with the values of Table 1, then the two angles  $\phi_{1-2}$  and  $\phi_{2-3}$  in GG(ag) could be refined independently, giving values not significantly

Table 9. Relative amounts of conformers of 1,2,3-tribromopropane at  $88^\circ\text{C}$ . Parameter correlation:  $\rho(\alpha_4/\alpha_2) = -0.84$ ,  $\alpha_4$  and  $\alpha_2$  are the composition parameters refined and  $\alpha_3 = 100 - \alpha_2 - \alpha_4$ ;  $\rho(\alpha_1/u_a) = -0.78$ ,  $\rho(\alpha_1/u_a) = 0.79$ , and  $u_a = u[\text{C}\cdots\text{X}(\text{anti})]$ .

Conformer	$\alpha$ (%)	$\sigma$	$\sigma_s$
(4); GG(ag) + GG(ga)	82	1	(0.5)
(3); GA(gg) + AG(gg)	8	2	(1.0)
(2); AG(ga) + GA(ag)	10	2	(1.0)

different from  $114.7^\circ$  and  $125.3^\circ$ . The calculated torsion angles of Table 1 are different from the experimental ones, however, the general agreement is quite good, and in both cases the value of  $\phi_A$  is seen to be larger than  $\phi_G$ .

The final composition parameters are presented in Table 9. The fact that conformers (4), (3), and (2) are present in detectable amounts, is well established. Moreover, it has also been demonstrated that conformers (1), (5), and (6) are not present in detectable amounts at  $88^\circ\text{C}$ .

Refined mean amplitudes of the most important internuclear distances are compared with calculated ones as summarized in Table 10.

Table 10. Mean amplitudes of vibration at  $88^\circ\text{C}$  for 1,2,3-tribromopropane. If a value is in parentheses it has been refined together with the preceding  $u$  value as one parameter.

Dist.	Least-squares $u$ value ( $\text{\AA}$ )	Calculated $u$ value ( $\text{\AA}$ )	$\sigma$	$\sigma_s$
C-H	0.074	0.078	0.009	(0.013)
C-C	0.051	0.051	0.006	(0.006)
$\text{C}_1-\text{X}_1$	0.051	0.055	0.005	(0.003)
$\text{C}_2-\text{X}_2$	(0.055)	0.059	-	(-)
$\text{C}_2\cdots\text{X}_1$	0.078	0.080	0.006	(0.002)
$\text{C}_1\cdots\text{X}_2$	(0.075)	0.077	-	(-)
in GG(ag)				
$\text{C}_1\cdots\text{X}_3(\text{g})$	0.181	0.149	0.025	(0.008)
$\text{C}_2\cdots\text{X}_1(\text{g})$	(0.197)	0.165	-	(-)
$\text{X}_1\cdots\text{X}_2(\text{a})$	0.070	0.081	0.004	(0.002)
$\text{X}_2\cdots\text{X}_3(\text{g})$	0.161	0.168	0.004	(0.003)
$\text{X}_1\cdots\text{X}_3$	0.281	0.279	0.008	(0.008)

The  $u$  values independently refined are in good agreement with those calculated using final torsional force constants. Several, less important, amplitude values could not be refined. These values have been adjusted along with the torsional force constants (Sect. V-B).

Probably the conformers (2) and (3) have torsional force fields not too different from the most abundant conformer, therefore, the average torsional force constant of conformer (4) was used in calculating  $u$  and  $K$  values for the conformers (2) and (3).

Correlation coefficients from least-squares refinements are summarized in Tables 6-9.

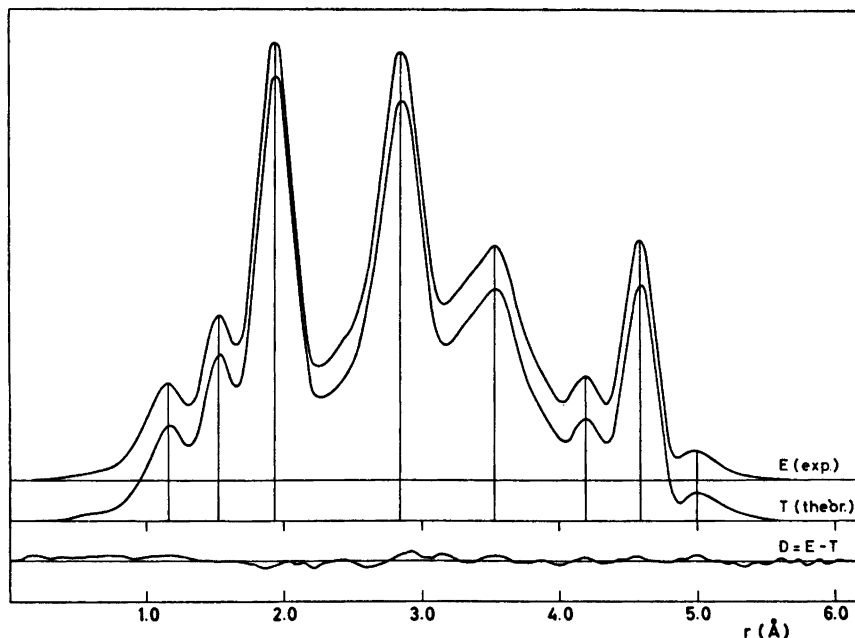


Fig. 8. Experimental (E) and theoretical (T) radial distribution curves and difference curve (D). The RD curves were calculated from the intensity curves of Fig. 5 with an artificial damping constant  $0.0020 \text{ \AA}^2$ .

It seemed out of place to report on all coefficients; only those with absolute values larger than 0.5 have been shown.

The theoretical intensity, corresponding to the final least-squares parameters, is shown in Fig. 5, and the RD curve in Fig. 8. The agreement between theoretical and experimental curves is very good, and only slightly better than the fit obtained with all  $u$  and  $K$  values calculated using the final force constants.

Cartesian coordinates for the GG(ag) conformer are given in Table 11. The principal axes' moments of inertia for the conformers (1), (2), (3), and (4) are also found in Table 11.

## VII. DISCUSSION

Recently, the NMR spectra of dilute solutions of TBP have been examined by Ernst and Schaefer.<sup>16</sup> From the three- and four-bond spin-spin coupling constants and from a comparison between observed and calculated dipole moments they concluded that in non-polar solvents TBP exists preferably in the enantiomeric conformations GG(ag) and GG(ga).

In polar solvents other conformers contribute to the equilibrium but still seem to play a minor role. The authors<sup>16</sup> emphasize that their conclusions can only be of a qualitative nature, nevertheless, their results are in good agreement with the present work.

An extensive study of the vibrational spectra of 1,2,3-trihalopropanes ( $X = \text{Br}, \text{Cl}$ ) have been carried out by Thorbjørnsrud, Ellestad, Klæboe, and Torggrimsen.<sup>7</sup> From the IR, far-IR, and Raman spectra alone it could not be concluded that (4) is the abundant conformer of the vapour phase. However, it was possible for Thorbjørnsrud *et al.*<sup>7</sup> to conclude that the most abundant conformer of the vapour phase also predominates in the liquids and is the preferred conformer in the crystals.

The torsional frequencies calculated, using the force field in Table 2 and torsional force constants determined from the diffraction data, are  $\omega_1 = 45 \pm 10 \text{ cm}^{-1}$  and  $\omega_2 = 86 \pm 10 \text{ cm}^{-1}$ .

The results reported by Thorbjørnsrud *et al.*<sup>7</sup> ( $\omega_1 = 97 \text{ cm}^{-1}$  and  $\omega_2 = 107 \text{ cm}^{-1}$ ) would lead to  $u$ -values very much smaller than those obtained by electron diffraction (Table 5).

Table 11. Cartesian coordinates for the GG(ag) conformer of 1,2,3-tribromopropane (see Fig. 2). The coordinates have been computed using the final structure parameters in Tables 6-8 and the numbering of atoms is shown in Fig. 2. The principal axes' moments of inertia ( $\text{amu } \text{Å}^2$ ) are:

Conformer (4):  $I_a = 569.12$ ,  $I_b = 948.75$ , and  $I_c = 1441.07$

Conformer (3):  $I_a = 387.13$ ,  $I_b = 1151.41$ , and  $I_c = 1446.09$

Conformer (2):  $I_a = 520.90$ ,  $I_b = 1140.77$ , and  $I_c = 1627.72$

Conformer (1):  $I_a = 297.64$ ,  $I_b = 1360.28$ , and  $I_c = 1573.24$

Torsion angles for AA(gg) were  $\phi_{1-2} = 12.2^\circ$  and  $\phi_{2-3} = -12.2^\circ$

Atom	X-Coord. (Å)	Y-Coord. (Å)	Z-Coord. (Å)
C <sub>3</sub>	0.0000	0.0000	0.0000
C <sub>1</sub>	1.3106	0.7972	0.0000
X <sub>1</sub>	1.4939	1.8011	-1.6593
H <sub>1</sub> '	1.3357	1.5287	0.8635
H <sub>1</sub>	2.2014	0.1056	0.0978
C <sub>2</sub>	-1.3106	0.7972	0.0000
X <sub>2</sub>	-1.3421	2.0508	1.4907
H <sub>2</sub> '	-1.4237	1.3841	-0.9613
H <sub>2</sub>	-2.2014	0.1056	0.0978
X <sub>3</sub>	0.0000	-1.3113	1.4405
H <sub>3</sub>	0.0000	-0.7120	-0.8800

Perhaps part of the discrepancy is due to the fact that the electron diffraction data are from the vapour phase, while the spectroscopic data are from the liquid phase. Moreover, the spectroscopic determination of frequencies below  $100 \text{ cm}^{-1}$  is very difficult. An error in assignment of low frequencies is not ruled out (see Table 3). The lowest frequency ( $45 \text{ cm}^{-1}$ ) could have escaped detection.

It is strongly felt that electron-diffraction data together with low frequencies from vibrational spectra, preferably from the gas phase, is really the combination needed for determining the torsional force constants in TBP and related molecules.

Following standard statistical thermodynamics,<sup>17</sup> the percentages  $\alpha$  and  $\alpha'$  for two conformers ( $C \rightleftharpoons C'$ ) in equilibrium in the gas phase, are related to the theoretical expression for the equilibrium constant, as given in eqn. (2):

$$\alpha'/\alpha = (Q'_{\text{rot}}/Q_{\text{rot}})(\sigma'/\sigma)^{-1}(Q'_{\text{vib}}/Q_{\text{vib}}) \exp(-\Delta E/RT) \quad (2)$$

If a pair of enantiomeric conformations are treated as *one* conformer, when computing equilibrium constants, that conformer must be assigned a statistical weight of two. If each of the *distinguishable* conformers are given a statistical weight equal to *one*, no problem should occur when the symmetry number  $\sigma$  is included in eqn. (2).

$Q_{\text{rot}}$  is the *classical* rotational partition function,<sup>18</sup>  $Q_{\text{rot}} \propto (I_a I_b I_c)^{3/2}$ , and the factor  $Q'_{\text{rot}}/Q_{\text{rot}}$  is very near to 1.0 for all combinations in TBP and similar molecules.

$Q_{\text{vib}}$  is the vibrational partition function,<sup>18</sup> referred to the *minimum* of potential energy, for a conformer.

$\Delta E = E' - E$  is the difference in potential energy between two conformers, and the difference is measured between energy *minima*.

$R$  and  $T$  have their usual thermodynamic meaning.

A considerable simplification of eqn. (2) is possible if the vibrational partition functions for the conformers are equal, or nearly equal. Eqn. (3) is the simplified form of eqn. (2).

$$\alpha'/\alpha = (\sigma'/\sigma)^{-1} \exp(-\Delta E/RT) \quad (3)$$

The approximation that  $Q'_{\text{vib}} = Q_{\text{vib}}$ , is not obvious for molecules like TBP. A moderate difference in torsional force constants alone will lead to values of  $Q'_{\text{vib}}/Q_{\text{vib}}$  quite different from 1.0, as shown in Table 5.

Experimental torsional force constants for conformer (4) are known, while the corresponding quantities for the remaining conformers are unknown. However, the energy calculations indicated that the average torsional force constants for the conformers (4), (3), and (2) are not very different.

If the approximation  $Q'_{\text{vib}} = Q_{\text{vib}}$  is assumed to be valid, the experimental differences in conformational energies might be calculated from eqn. (3). These calculations lead to the conclusions that the conformers (2) and (3) are nearly *equal* in energy and about  $1.5 \pm 0.4$  kcal/mol *less* stable than conformer (4).

The theoretical energy calculations (Table 1) gave the answer that conformer (4) was *less* stable, about 0.6 kcal/mol, than conformer (2). The two values  $-1.5$  and  $+0.6$  for  $\Delta E = E_4 - E_2$

do not agree. Could the disagreement be explained by a difference in vibrational partition functions between the two conformers? If that was the explanation, the ratio between the functions had to be about 18, but no reasonable values of torsional force constants, or other force constants, could lead to such a large ratio.

Moreover, similar disagreements were encountered in 1,3-dibromopropane<sup>21</sup> as well as in 1,2,3-trichloropropane.<sup>21</sup>

The discrepancy can not easily be explained in terms of simple adjustments in the applied force field. In the vapour phase, it seems that the GG conformer of low energy is always more stable than any other conformer in this type of molecules, also including 3-chloro-1-propanol investigated by Bastiansen *et al.*<sup>19</sup>

Additional information<sup>20</sup> about the thermodynamic equilibrium quantities, and the geometry of the conformers (2) and (3), may be obtained by studying TBP at higher temperatures. The expected composition at 200°C is approximately  $\alpha_4 = 50\%$  and  $\alpha_2 = \alpha_3 = 25\%$ .

*Acknowledgements.* I am grateful to Cand.real. A. Almenningen for recording the diffraction photographs, and to Professor O. Bastiansen, Professor S. J. Cyvin, Professor J. Dale, Cand.real. O. Ellestad, Dr. A. Haaland, Dr. P. Klæboe, and Dr. H. M. Seip for helpful discussions. Computer programs made available by Dr. H. M. Seip, Cand.real. S. Rustad, and Professor W. D. Gwinn have been extensively used in this work. Financial support from Norges almenvitenskapelige forskningsråd is gratefully acknowledged.

## REFERENCES

1. Abraham, R. J. and Parry, K. J. *J. Chem. Soc. B* (1970) 539.
2. Rustad, S. *Thesis, at Oslo University*, Oslo 1973.
3. Allinger, N. L., Hirsch, J. A., Miller, M. N., Tyminski, I. J. and Van-Catledge, F. A. *J. Amer. Chem. Soc.* 90 (1968) 1199.
4. Schachtneider, J. H. and Snyder, R. G. *Vibrational Analysis of Polyatomic Molecules. IV* (force constants for the haloparaffins) Project No. 31450, Technical Report No. 122-63 of Shell Development Company.
5. Snyder, R. G. *J. Mol. Spectrosc.* 28 (1960) 273.
6. Gwinn, W. D. *J. Chem. Phys.* 55 (1971) 477.
7. Thorbjørnsrud, J., Ellestad, O. H., Klæboe, P. and Torgrimsen, T. *J. Mol. Struct.* 17 (1973) 5.
8. Stølevik, R., Seip, H. M. and Cyvin, S. J. *Chem. Phys. Lett.* 15 (1972) 263.
9. Bastiansen, O., Hassel, O. and Risberg, E. *Acta Chem. Scand.* 9 (1955) 232.
10. Andersen, B., Seip, H. M., Strand, T. G. and Stølevik, R. *Acta Chem. Scand.* 23 (1969) 3224.
11. Peacher, J. and Willis, J. C. *J. Chem. Phys.* 46 (1967) 4809.
12. Strand, T. G. and Bonham, R. A. *J. Chem. Phys.* 40 (1964) 1686.
13. Morino, Y., Kuchitsu, K. and Oka, T. *J. Chem. Phys.* 36 (1962) 1108.
14. Kuchitsu, K. *J. Chem. Phys.* 49 (1968) 4456.
15. Seip, H. M. and Stølevik, R. In Cyvin, S. J., Ed., *Molecular Structure and Vibrations*, Elsevier, Amsterdam 1972.
16. Ernst, L. and Schaefer, T. *Can. J. Chem.* 51 (1973) 565.
17. Seip, H. M. In Sim, G. A. and Sutton, L. E., Eds., *Molecular Structure by Diffraction Methods* (Specialist Periodical Reports), The Chemical Society, London 1973, Vol 1, Part 1, Chapter 1.
18. Herzberg, G. *Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand, Princeton.
19. Bastiansen, O., Brunvoll, J. and Hargittai, I. In Cyvin, S. J., Ed., *Molecular Structure and Vibrations*, Elsevier, Amsterdam 1972.
20. Almenningen, A., Bastiansen, O., Fernholt, L. and Hedberg, K. *Acta Chem. Scand.* 25 (1971) 1946.
21. Fårup, P. E. and Stølevik, R. *Acta Chem. Scand.* To be published.

Received October 15, 1973.