

# Conformational Analysis. V. The Molecular Structure, Torsional Oscillations, and Conformational Equilibria of Gaseous 1,3-Dibromopropane, $(\text{CH}_2\text{Br})_2\text{CH}_2$ , as Determined by Electron Diffraction and Compared with Semi-empirical (Molecular Mechanics) Calculations

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Gaseous 1,3-dibromopropane has been studied by electron diffraction at a nozzle temperature of 65 °C. Three spectroscopically distinguishable conformers *GG*, *AG*, and *AA* (see Fig. 1) were detected. Results are presented with error limits ( $2\sigma$ ). The following values for bond lengths ( $r_a$ ) and bond angles ( $\angle\alpha$ ) are average parameters for the conformers:  $r(\text{C}-\text{H}) = 1.126(18)$  Å,  $r(\text{C}-\text{C}) = 1.527(10)$  Å,  $r(\text{C}-\text{Br}) = 1.959(4)$  Å,  $\angle\text{CCC} = 111.4^\circ (3.2)$ , and  $\angle\text{CCBr} = 112.0^\circ (0.6)$ . Non-bonded distances were computed as dependent quantities under the constraints of geometrically consistent  $r_a$  parameters.

By symmetry *AA* has a staggered conformation. The conformers *AG* and *GG* have torsion angles close to staggered values (Table 11).

The relative amounts of the conformers have been determined, and the composition at 65 °C is: 67 % (4) of *GG*, 30 % (4) of *AG*, and 3 % (4) of *AA*. The radial distribution curves show that a small relative amount of *AA* is present, in spite of the large error limit (4 %) estimated by the least-squares procedure. The conformer with two C—Br bonds parallel, *GG*(1:3), is not present in detectable amounts. According to the semiempirical calculations, *AA* is the conformer of lowest minimum energy, but this result is only possible if the zero-point vibrational energies of *GG* and *AG* are significantly smaller than that of *AA*. This question has been discussed.

Torsional force constants and frequencies corresponding to torsional modes have been estimated by combining information from electron diffraction and vibrational spectroscopy. The spectroscopic assignment of low frequencies for the conformer *GG* has to be changed in order to get agreement with the vibrational quantities determined by electron diffraction. A new assignment has been proposed.

## I. INTRODUCTION

The present electron diffraction work is part of a systematic conformational study of halo-generated propanes and related molecules. General <sup>1</sup> information <sup>2</sup> relevant to this investigation and to the electron diffraction method <sup>3</sup> is found in Refs. 1—3.

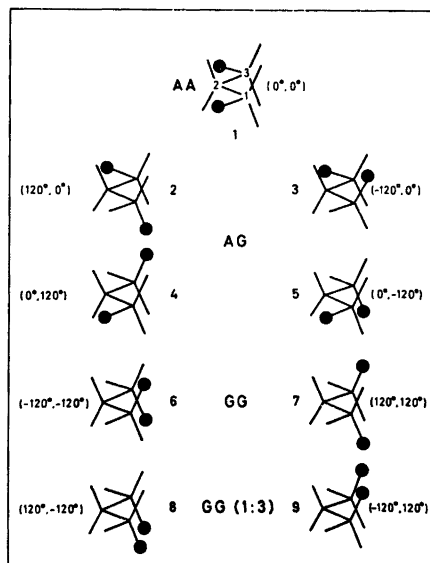


Fig. 1. The numbering and names of staggered conformers in 1,3-dibromopropane. The torsion angles ( $\phi_{1-2}$ ,  $\phi_{2-3}$ ) are shown in parentheses.

**Table 1.** Characterization of the four spectroscopically distinguishable staggered conformers of 1,3-dihalopropane. Classically there are *nine* possible staggered conformers. *Six* of the conformers are distinguishable, but only *four* are spectroscopically distinguishable (see Fig. 1).

Conformer	Point group	Symmetry number ( $\sigma$ )	$M_c$	$M_d$	$2(M_d/\sigma)$
<i>AA</i>	$C_{2v}$	2	1	1	1
<i>AG</i>	$C_1$	1	4	2	4
<i>GG</i>	$C_s^*$	2	2	2	2
<i>GG(1:3)</i>	$C_s$	1	2	1	2

Compounds of the type  $(CH_2X)_2CH_2$  will be referred to as DXP ( $X = F, Cl, Br, I$ ), and the title compound as DBP. Classically the possible number of staggered conformers in DXP is *nine*, as indicated in Fig. 1. The conformer 6 and 7 are *enantiomers* and thereby physically distinguishable, but neither spectroscopy nor electron diffraction can distinguish between them. The conformers 8 and 9 are identical in all respects. The conformers 2 and 3 are enantiomers, while 4 and 5 are identical to 2 and 3, respectively. In conclusion, there are *six* physically different conformers, but only *four* [*AA*, *AG*, *GG*, and *GG(1:3)*] are spectroscopically distinguishable, as indicated in Fig. 1 and Table 1.

Whenever torsion-angle dependent quantities have to be specified, the conformers 1, 2, 7, and

8 will be taken to represent *AA*, *AG*, *GG*, and *GG(1:3)*, respectively.

There are four  $X \cdots X$  distances of different lengths: *AA* (*anti-anti*), *AG* (*anti-gauche*) *GG* (*gauche-gauche*), and *GG(1:3)* which corresponds to a parallel  $(1:3)X \cdots X$  interaction. The symbols *A* (*anti*) and *G* (*gauche*) thus refer to the plane of the CCC atoms (see Fig. 1).

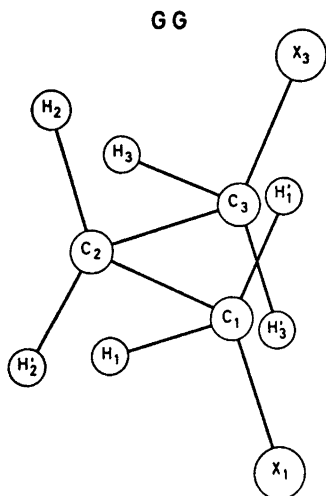
The spectroscopically distinguishable conformers may be assigned multiplicities in two ways, as follows:

(1) only conformers being distinguishable (*six*) are considered. ( $M_d$  in Table 1).

(2) all classically possible conformers (*nine*) are included. ( $M_c$  in Table 1).

It is noteworthy<sup>4</sup> that  $M_c^*/M_c = (M_d^*/M_d) \times (\sigma^*/\sigma)^{-1}$  for two spectroscopically distinguishable conformers, C and C\*, having symmetry numbers  $\sigma$  and  $\sigma^*$ .

Brown and Sheppard<sup>5</sup> and later on Dempster, Price, and Sheppard<sup>6</sup> studied DBP by vibrational spectroscopy. Based upon infrared spectra they concluded that DBP crystallizes in the *GG* conformation at low temperatures. An extended vibrational spectral study of DBP as liquid, in solution, and in the crystalline state at low temperatures and at high pressure has been published by Thorbjørnsrud *et al.*<sup>7</sup> The three conformers *GG*, *AG*, and *AA* were observed in the liquid. They also found that DBP crystallizes in the *GG* conformation at high pressure.



**Fig. 2.** Numbering of atoms in the conformer *GG* of 1,3-dibromopropane.

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

(Molecular Mechanics Calculations)

The semiempirical energy calculations were carried out as described in Ref. 8. Energy parameters ( $V_0$ ,  $a$ ,  $b$ ,  $c$ ,  $d$ ) were taken from the work of Abraham and Parry,<sup>8</sup> and diagonal valence force constants from Table 2 were used. "Normal" values of the geometry parameters are given in Table 2.

The conformational geometries derived from the semiempirical energy model are presented in Table 2. According to the results in Table 2, *GG* and *AG* have nearly staggered conformations, while *AA* is exactly staggered. Small differences in bond angles and practically no

Table 2. Calculated conformational geometries for 1,3-dibromopropane. Distances in Å, angles in deg.

Parameter (normal value)	GG	AG	AA	GG(1:3)
$r(\text{C}-\text{H})$ , (1.094)	1.094	1.094	1.094	1.094
$r(\text{C}-\text{C})$ , (1.513)	1.524	1.522	1.520	1.527
$r(\text{C}-\text{X})$ , (1.935)	1.940	1.939	1.937	1.940
$\angle \text{CCC}$ (110.0)	113.3	112.0	110.7	113.9
$\angle \text{CCX}$ (109.47)	110.9	110.5	110.0	112.4
$\angle \text{CC}_2\text{H}$ (109.47)	108.9	109.1	109.3	108.8
$\angle \text{C}_2\text{CH}$ (109.47)	109.9	109.8	109.8	109.6
$\phi_{1-2}^a$	112.7	113.2	0.0	(98.0) <sup>b</sup>
$\phi_{3-2}^a$	112.7	3.0	0.0	(-98.0) <sup>b</sup>

In minimizing the energy the geometry was constrained as described in Sect. V-A: <sup>a</sup>  $\phi_0 = 60^\circ$  in the expression  $V\phi = \frac{1}{2}V_0 \sum_k (1 + \cos[3(\phi_{k-2} - \phi_0)])$ ,  $k=1, 3$ . <sup>b</sup> The conformer GG(1:3) does not correspond to a well defined energy minimum (see also Table 4).

Table 3. Conformational energies (kcal/mol) for 1,3-dibromopropane. Details about the energy expression are found in Ref. 8. Zero-point vibrational energies for the conformers are not included.

Type of energy	GG	AG	AA	GG(1:3)
$E$ (bonded)	0.69	0.35	0.08	2.58
$E$ (van der Waals)	0.90	0.77	0.57	1.35
$E$ (polar, X...H)	-5.65	-5.50	-5.29	-5.20
$E$ (polar, X...X)	1.48	1.30	1.16	1.87
$E$ (total)	-2.58	-3.09	-3.47	0.60
$E$ (total) - $E(\text{AA}) = \Delta E^m$	0.89	0.38	0.00	4.07

Table 4. Conformational energies and torsional barriers in 1,3-dibromopropane. Details about the conformational minima corresponding to the stable conformers AA, AG, and GG are found in Table 2 and Table 3.

$\phi_{1-2}$ $\phi_{2-3}$	(-180°)	(-120°)	(-60°)	(0°)	(60°)	(120°)	(180°)
(180°)	∞	8.5	12.2	5.6	12.2	8.5	∞
(120°)	8.5	GG(1:3) 4.1	4.1	AG 0.4	3.6	GG 0.9	8.5
(60°)	12.2	4.1	7.7	3.5	7.5	3.6	12.2
(0°)	5.6	AG 0.4	3.5	AA 0.0	3.5	AG 0.4	5.6
(-60°)	12.2	3.6	7.5	3.5	7.7	4.1	12.2
(-120°)	8.5	GG 0.9	3.6	AG 0.4	4.1	GG(1:3) 4.1	8.5
(180°)	∞	8.5	12.2	5.6	12.2	8.5	∞

differences in bond lengths, between the conformers, are predicted by these calculations.

According to the calculated conformational energies of Table 3, AA is the most stable conformer. The conformer GG(1:3), which does not

correspond to a well defined energy minimum (see Table 4), is ca. 4 kcal/mol less stable than AA.

Conformational energy minima and torsional barriers between the conformers are shown in

Table 5. Calculated torsional force constants for 1,3-dibromopropane.

$F_\phi = \partial^2 E / \partial \phi^2$  and  $F_{\phi\phi'} = \partial^2 E / \partial \phi \partial \phi'$  were numerically computed.

(mdyn Å(rad) <sup>-2</sup> )	GG	AG	AA
$F_\phi(1-2)$	0.159	0.141	0.114
$F_\phi(3-2)$	0.159	0.114	0.114
$F_{\phi\phi'}(1-2,3-2)^*$	-0.038	-0.033	-0.009

Table 4. Each energy value has been obtained by adjusting *all* geometry variables except for the values of  $\phi_{1-2}$  and  $\phi_{2-3}$  being  $\pm 60^\circ$  or  $\pm 180^\circ$ . Such values of the torsion angles correspond to eclipsed conformations.

The torsional force constants given in Table 5 were numerically computed. The calculated values here are too low compared to the experimentally determined values of Sect. V-B.

### III. CALCULATION OF VIBRATIONAL QUANTITIES

Valence force constants, except for the torsional part, were taken from works of Schacht-

schneider<sup>10</sup> and Snyder.<sup>11</sup> The final force constant values used here are shown in Table 6.

Since observed frequencies are available,<sup>7</sup> it is possible to adjust most force constants of Table 6 to fit DBP 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. Mean amplitudes ( $u$  and  $K$  values) of DBP are quite insensitive to moderate errors in the force field, except for the torsional part of it, which has been adjusted (Sect. V-B). Moreover, it is important to use typical force constants as much as possible in order to test the transferability in various situations. The works by Schachtschneider<sup>10</sup> and Snyder<sup>11</sup> in this respect are extremely valuable for electron diffraction studies.

The normal-coordinate program described by Gwinn<sup>12</sup> was used in computing vibrational frequencies (Table 7). The fit between observed spectroscopic frequencies and those calculated is good. If the first three ( $\omega_1$ ,  $\omega_2$ , and  $\omega_3$ ) frequencies are left out, the deviation between the

Table 6. Valence force constants for 1,3-dibromopropane.

Stretch (mdyn Å <sup>-1</sup> )		Bend [mdyn Å (rad) <sup>-2</sup> ]	
C-C	4.73	CCC	0.90
C <sub>1</sub> -H	4.85	CCH	0.67
C <sub>2</sub> -H	4.55	HCH	0.53
C-X	2.63	CCX	0.91
		HCX	0.69
Stretch/Stretch (mdyn Å <sup>-1</sup> )		Stretch/Bend [mdyn(rad) <sup>-1</sup> ]	
(C-C common)		(C-X common)	
C-X/C-C	0.35	C-X/CCX	0.49
C-C/C-C	0.064	C-X/HCX	0.26
		(C-C common)	
Bend/Bend (mdyn Å (rad) <sup>-2</sup> )		C-C/CCX	0.30
(C-C common)		C-C/CCC	0.29
HCC/CCC	-0.12	C-C/CCH	0.26
Torsion [mdyn Å (rad) <sup>-2</sup> ]			
Conformer:	GG	AG	AA
$F_\phi(1-2)^a$	0.243	0.225	0.198
$F_\phi(2-3)^a$	0.243	0.198	0.198

<sup>a</sup> The torsional force constants have been defined as follows: each fragment A'-C<sub>1</sub>-C<sub>2</sub>-A'' (A=H, C, X, see Fig. 2) has been assigned an equal force constant. Each fragment A'-C<sub>2</sub>-C<sub>3</sub>-A'' has been assigned an equal force constant, but generally different from those of fragments A'-C<sub>1</sub>-C<sub>2</sub>-A''. The total force constant for the torsional coordinate  $\phi_{i-2}$  (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.

Table 7. Vibrational frequencies in 1,3-dibromopropane. The valence force field of Table 6 was used.

Approximate mode	Spectroscopic value (GG) <sup>7</sup>	GG	AG	AA
Torsion ( $\omega_1$ )	176	47	71	100
Torsion ( $\omega_2$ )	186	149	107	115
CCX bend ( $\omega_3$ )	310	189	214	159
CCX bend ( $\omega_4$ )	324	371	266	220
CCC bend	425	420	358	342
C-X stretch	549	566	570	581
C-X stretch	591	578	649	705
CH <sub>2</sub> rock	763	805	807	812
CH <sub>2</sub> rock	854	849	844	820
C-C stretch	958	996	984	996
CH <sub>2</sub> rock	943	1018	1019	1024
C-C stretch	1073	1104	1094	1082
CH <sub>2</sub> twist	1122	1195	1205	1210
CH <sub>2</sub> twist	1133	1215	1223	1219
CH <sub>2</sub> twist	1240	1243	1239	1252
CH <sub>2</sub> wag	1232	1317	1306	1285
CH <sub>2</sub> wag	1294	1321	1322	1342
CH <sub>2</sub> wag	1349	1351	1349	1346
CH <sub>2</sub> scissor	1417	1453	1441	1433
CH <sub>2</sub> scissor	1430	1454	1453	1450
CH <sub>2</sub> scissor	1450	1519	1516	1520
C-H stretch	2850	2817	2817	2817
C-H stretch	2908	2955	2955	2956
C-H stretch	2924	2956	2956	2956
C-H stretch	2969	2962	2961	2960
C-H stretch	3010	3008	3008	3009
C-H stretch	3010	3010	3009	3009

two sets is less than 3 %. (See also discussion in Sect. VII.)

Mean amplitudes of vibration were computed as described in Ref. 13. In Table 8 are given  $u$  and  $K$  values for internuclear distances.

Some of these quantities are quite sensitive to the values of the torsional force constants, which have been adjusted to fit the experimental intensities (Sect. V-B). In Table 9 are shown vibrational quantities corresponding to different values of the torsional force constants.

#### IV. EXPERIMENTAL AND DATA REDUCTION

A commercial sample of DBP was obtained from Fluka. The sample was purified by distillation under reduced pressure.<sup>7</sup> The final purity was ca. 99 %.

Electron-density photographs were made at a nozzle temperature of 65 °C in the Balzer<sup>14</sup> apparatus<sup>15</sup> under conditions summarized below:

Nozzle-to-plate distance (mm)	500	250
Electron wavelength (Å)	0.05848	0.05845
Number of plates	5	5
Range of data, in $s(\text{Å}^{-1})$	1.125–14.75	2.25–21.00
Data interval, $\Delta s(\text{Å}^{-1})$	0.125	0.250
Uncertainty in $s$ -scale (%)	0.14	0.14

The electron wavelength was determined by calibration against ZnO and corrected by an experiment with CO<sub>2</sub> giving a correction of

Table 8. Mean amplitudes of vibration in 1,3-dibromopropane at 65 °C.

Type of distance	Dist. <sup>a</sup> (Å)	Conformer <i>GG</i> <sup>b</sup> <i>u</i> (Å)	<i>K</i> (Å)	Conformer <i>AG</i> <sup>b</sup> <i>u</i> (Å)	<i>K</i> (Å)
C <sub>2</sub> -H	(1.11)	0.0792	0.0166	0.0792	0.0210-4 <sup>c</sup>
C <sub>1</sub> -H	(1.11)	0.0780	0.0213-23 <sup>c</sup>	0.0780	0.0189-93 <sup>c</sup>
C <sub>3</sub> -H	(1.11)	0.0780	0.0213-23 <sup>c</sup>	0.0780	0.0285-96 <sup>c</sup>
C <sub>1</sub> -C <sub>2</sub>	(1.52)	0.0505	0.0056	0.0505	0.0073
C <sub>2</sub> -C <sub>3</sub>	(1.52)	0.0505	0.0056	0.0505	0.0099
C <sub>1</sub> -X	(1.95)	0.0546	0.0130	0.0547	0.0075
C <sub>3</sub> -X	(1.95)	0.0546	0.0130	0.0546	0.0154
C <sub>2</sub> ···X	(2.88)	0.0761	0.0080	0.0760	0.0066
C <sub>2</sub> ···H	(2.22)	0.1054	0.0153	0.1054	0.0214
C···C	(2.52)	0.0751	0.0054	0.0751	0.0085
C···H <sub>2</sub>	(2.09)	0.1098	0.0119	0.1099	0.0185
H <sub>1</sub> ···X <sub>1</sub> '	(2.49)	0.1130	0.0227	0.1131	0.0229
H <sub>1</sub> ···H <sub>1</sub> '	(1.75)	0.1292	0.0301	0.1293	0.0317
H <sub>2</sub> ···H <sub>2</sub> '	(2.00)	0.1197	0.0203	0.1199	0.0290
X···H( <i>anti</i> )	(3.83)	0.1064	0.0098	0.1071	0.0099
X···H( <i>gauche</i> )	(2.83)	0.1678	0.0114	0.168-72 <sup>c</sup>	0.009-13 <sup>c</sup>
X···C( <i>gauche</i> )	(3.33)	0.1575	0.0062	0.1608	0.0081
X···C( <i>anti</i> )	(4.26)	-	-	0.0777	0.0019
X···X( <i>GG</i> ) <sup>d</sup>	(4.41)	0.2680	0.0000	-	-
X···X( <i>AG</i> ) <sup>d</sup>	(5.13)	-	-	0.1656	0.0000
X···H( <i>GG</i> ) <sup>d</sup>	(2.90-5)	0.2525	0.0170	0.2548	0.0249
X···H( <i>AG</i> ) <sup>d</sup>	(4.3-6)	0.1865	0.0082	0.1723	0.0044
X···H( <i>AG</i> ) <sup>d</sup>	(3.53)	-	-	0.2685	0.0143
X···H( <i>AA</i> ) <sup>d</sup>	(5.09)	-	-	0.1240	0.0040

<sup>a</sup> The distances here correspond to a set of cartesian coordinates slightly different from those in Table 13.

<sup>b</sup> The valence force field of Table 6 was used. <sup>c</sup> The range of values corresponding to distances of this kind has been given. <sup>d</sup> *A(anti)* and *G(gauche)*. The combination X···H(*AG*) thus represents the X···H distance of a fragment X-C-C-C-H having one of the end bonds *anti*(A) and the other one *gauche*(G) to the CCC framework. The longest X···H(*AG*) distance has C-X *anti*.

+0.1 % in the *s*-scale. The data were reduced in the usual way<sup>16</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. The final experimental intensity curve is shown in Fig. 3. The intensities have been modified by  $s/|f_{Br}'||f_C'|$ .

Scattering amplitudes were calculated by the partial wave method<sup>17</sup> using Hartree-Fock atomic potentials.<sup>18</sup>

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

The radial distribution (RD) curve, obtained by Fourier transformation<sup>18</sup> of the final experimental intensity, is presented in Fig. 4.

## V. STRUCTURE ANALYSIS

Radial distribution (RD) curves for the conformers *GG*, *AG*, *AA*, and the experimental curve, are shown in Fig. 5. The conformers *GG*

and *AG* are clearly present in considerable amounts, and *GG* is the most abundant conformer. The small peak in the experimental RD curve at *ca.* 5.75 Å corresponds to a small contribution from the X···X distance of the conformer *AA*. Approximate composition parameters ( $\alpha$ ) were estimated from these RD curves:  $\alpha(\text{GG}) \simeq 60-70\%$ ,  $\alpha(\text{AG}) \simeq 20-40\%$ , and  $\alpha(\text{AA}) \simeq 0-10\%$ .

Theoretical RD curves corresponding to 0, 3, and 9 % of the conformer *AA*, are shown in Fig. 6 together with the final experimental curve. The conformer *AA* is clearly present in detectable amounts at 65 °C.

*A. Least-squares analysis.* The least-squares program was written by H. M. Seip, and it is a modified version of the program explained in Ref. 16. Several conformers may be included in the refinements with the present version of the program. Models for the conformers were

Table 9. Vibrational quantities in 1,3-dibromopropane at 65 °C.

Torsional force constant <sup>a</sup>			
$F_{\phi}(1-2) = F_{\phi}(2-3) = \bar{F}_{\phi}$ [mdyn Å(rad) <sup>-2</sup> ]	0.120	0.243	0.480
Torsional frequencies for the conformer <i>GG</i> (cm <sup>-1</sup> ) <sup>b</sup>			
	33	47	57
	125	149	181
Ratios ( <i>q</i> ) <sup>c</sup> between vibrational partition functions <sup>d</sup>			
$Q_{GG}(0.24)/Q_{AG}(\bar{F}_{\phi})$	0.33	1.17	5.48
$Q_{GG}(0.24)/Q_{AA}(\bar{F}_{\phi})$	0.33	1.17	5.48
$Q_{AG}(0.24)/Q_{AA}(\bar{F}_{\phi})$	0.28	1.00	4.68
Mean amplitudes ( <i>u</i> values) <sup>e</sup> for the X··X distance (Å)			
in conformer <i>GG</i>	0.386	0.268	0.232
in conformer <i>AG</i>	0.203	0.166	0.159
in conformer <i>AA</i>	0.113	0.113	0.112
<i>u</i> value <sup>e</sup> for the distance C··X ( <i>gauche</i> ) (Å)			
in <i>GG</i> and <i>AG</i>	0.187	0.159	0.144

<sup>a</sup> The remaining force constants are found in Table 6. <sup>b</sup> See also Table 7. <sup>c</sup> The differences in zero-point vibrational energy are included in the *q* values. <sup>d</sup> *Q*: vibrational partition function. <sup>e</sup> See also Table 8.

constructed with the following geometrical assumptions: (1) the two C-CH<sub>2</sub>X groups are equal; (2) each C-CH<sub>2</sub>X group possess *C*<sub>s</sub> symmetry; (3) the plane of the H<sub>2</sub>C<sub>2</sub>H<sub>2</sub>' group is perpendicular to the C-atom plane and bisects the CCC angle; (4) all C-H bonds are equal;

(5) the conformers have identical structures except for the C-C torsion angles ( $\phi_{1-2}$  and  $\phi_{2-3}$ ). The models were defined in terms of the following average parameters: *r*(C-H), *r*(C-C), *r*(C-X), ∠CCC, ∠C<sub>2</sub>CX, ∠C<sub>2</sub>CH, ∠CC<sub>2</sub>H,  $\phi_{1-2}$ ,  $\phi_{2-3}$ , and ∠(HC<sub>1</sub>H')\* which is the projec-

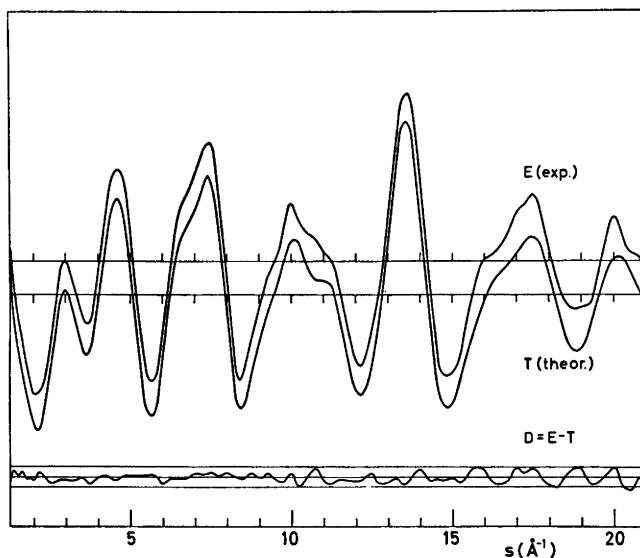


Fig. 3. Intensity curves for 1,3-dibromopropane at 65 °C. Experimental (E) and theoretical (T) intensity curves corresponding to the final least-squares parameters, and  $D = E - T$ . The straight lines give the experimental uncertainties ( $\pm 3 \times$  experimental standard deviation).

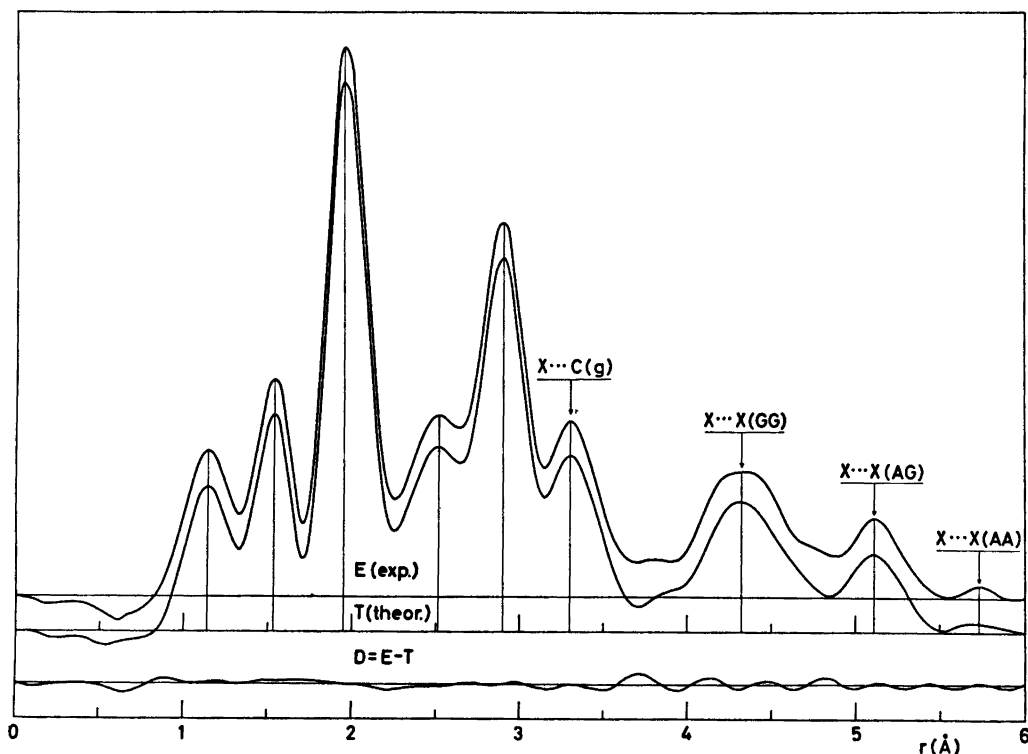


Fig. 4. Radial distribution curves for 1,3-dibromopropane at 65 °C. Experimental (E) and theoretical (T) radial distribution curves, and  $D = E - T$ . The RD curves were calculated from the intensity curves of Fig. 3 with an artificial damping constant of  $0.0020 \text{ \AA}^2$ .

tion of the  $\text{HC}_1\text{H}'$  angle on a plane perpendicular to the  $\text{C}_2 - \text{C}_1$  axes. Also adjusted were the composition (%) parameters  $\alpha(\text{GG})$  and  $\alpha(\text{AG})$  with  $\alpha(\text{AA}) = 100\% - \alpha(\text{GG}) - \alpha(\text{AG})$ .

Corrections for the "Bastiansen-Morino" shrinkage<sup>19</sup> effect on non-bonded distances have been included. Non-bonded distances were computed as dependent parameters, restricted under the constraints of geometrically consistent  $r_\alpha$  parameters.<sup>20,21</sup>

**B. Determination of torsional force constants.** The torsional modes of vibration contribute substantially to the mean amplitudes (Sect. III) of several internuclear distances in a molecule like DBP. Since a reasonable force field was known, except for the torsional part, torsional force constants can be adjusted to fit the electron-diffraction data. Determination of all torsional force constants from electron-diffraction data alone is not possible. The values in Table 5 were used as a guide, and the following assumptions were made:

$[F_\phi \text{ in m dyn } \text{\AA} (\text{rad})^{-2}] F_{\phi\phi'}(1-2; 3-2) = 0$  for all conformers.

in GG:  $F_\phi(1-2) = F_\phi(2-3) = 0.159 + \Delta F_\phi$

in AG:  $F_\phi(1-2) = 0.141 + \Delta F_\phi$ ,  $F_\phi(2-3) = 0.114 + \Delta F_\phi$

in AA:  $F_\phi(1-2) = F_\phi(2-3) = 0.114 + \Delta F_\phi$

$\Delta F_\phi$  was considered as a variable to be adjusted.  $K$  values and  $u$  values were computed for several values of  $\Delta F_\phi$  and then included in the least-squares refinements. The structure and composition parameters were adjusted for each new value of  $\Delta F_\phi$ . The best fit between experimental and theoretical intensities was obtained for  $\Delta F_\phi = 0.084$ , corresponding to the lowest value of the error sum  $(\mathbf{V}'\mathbf{P}\mathbf{V})$ .<sup>16</sup> A slight improvement was obtained if individual  $u$  values were refined (Sect. VI).

The error limits of  $\Delta F_\phi$  were estimated by direct inspection of the fit between theoretical and experimental RD curves computed for each value of  $\Delta F_\phi$ . Keeping in mind the assumptions



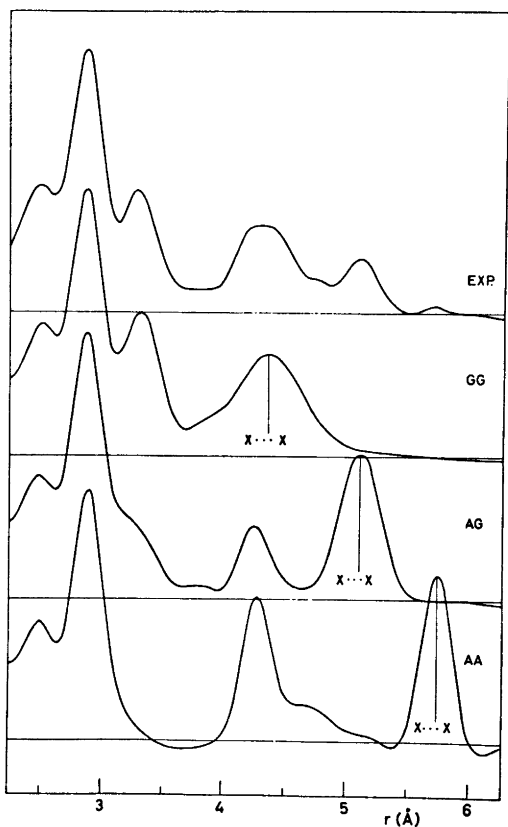


Fig. 5. Radial distribution curves for conformers of 1,3-dibromopropane at 65 °C. Theoretical RD curves of the conformers *AA*, *AG*, and *GG* are shown together with the final experimental curve. The artificial damping constant was equal to 0.0020 Å<sup>2</sup>.

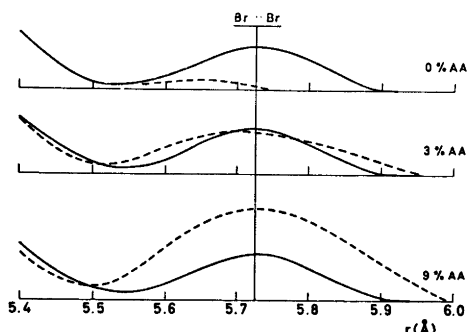


Fig. 6. Radial distribution curves for 1,3-dibromopropane at 65 °C. Experimental and theoretical (---) RD curves, computed with the ratio  $\alpha(GG)/\alpha(AG) = 67/30$  for the theoretical curves. An artificial damping constant equal to 0.0020 Å<sup>2</sup> was used.

above, the most probable values of the torsional force constants [ $\text{mdyn } \text{Å} (\text{rad})^{-2}$ ] are:

$$F_{\phi}(1-2) = F_{\phi}(2-3) = 0.243 \begin{matrix} +0.10 \\ -0.05 \end{matrix}$$

in conformer *GG*

$$F_{\phi}(1-2) = 0.225 \begin{matrix} +0.10 \\ -0.05 \end{matrix} \text{ and } F_{\phi}(2-3) = 0.198$$

+0.10  
-0.05 in conformer *AG*

$$F_{\phi}(1-2) = F_{\phi}(2-3) = 0.198 \begin{matrix} +0.10 \\ -0.05 \end{matrix}$$

in conformer *AA*

(The conformational *differences* in the torsional force constants thus correspond to the theoretical values of Table 5.)

The present electron-diffraction data do not justify any further adjustment of torsional force constants. However, the value of  $F$  (0.243) for *GG* seems reasonable compared to the values determined for the conformer *GG* (*ag*) of 1,2,3-tribromopropane<sup>8</sup> ( $\bar{F}_{\phi} = 0.30$ ,  $F_{\phi}(1-2) = 0.20$  and  $F_{\phi}(2-3) = 0.40$ ).

## VI. FINAL RESULTS

Parameters from the least-squares refinements<sup>16</sup> and standard deviations ( $\sigma$ ) corrected for correlation in the experimental data<sup>22</sup> are given. In the final refinements, intensities beyond  $s = 21.00 \text{ Å}^{-1}$  were not included and, using a diagonal weight matrix, all intensities were given equal weights.

Non-bonded distances were restricted under the geometrical constraints of  $r_{\alpha}$  parameters, by including correction terms  $D = r_{\alpha} - r_a$  ( $D = u^2/r - K$ ) for all distances.

Parameter correlation coefficients ( $\rho$ )<sup>16</sup> with  $|\rho| > 0.49$  are included in Tables 10–12. Bond lengths and bond angles are found in Table 10. Torsion angles and composition parameters are found in Table 11.

The value of  $\angle \text{CCC} = 111.4^\circ$  seems somewhat low compared with the calculated values of  $113.3^\circ$  (*GG*) and  $112.0^\circ$  (*AG*), but the uncertainty ( $\sigma = 1.6^\circ$ ) of this parameter does not exclude values as large as  $113-114^\circ$ .

Within their standard deviations the torsion angles of Table 11 agree with those calculated according to the semiempirical energy model (Table 2), and the deviation from staggered values are significant at least for the conformer *GG*.

Table 10. Average bond lengths (Å) and bond angles (deg.) in the conformers of 1,3-dibromopropane. Standard deviations are given in parenthesis.

Bond lengths ( $r_a$ ) <sup>a</sup>	Bond angles ( $\angle\alpha$ ) <sup>b</sup>
$r_a(\text{C}-\text{H}) = 1.126(9)$	$\angle\text{CCC} = 111.4(1.6)$ $\angle\text{C}_2\text{CBr} = 112.0(0.3)$
$r_a(\text{C}-\text{C}) = 1.527(5)$	$\angle\text{C}_2\text{CH} = 115.4(3.6)^c$ $\angle\text{CC}_2\text{H} = 103.0(2.0)^c$
$r_a(\text{C}-\text{Br}) = 1.959(2)$	$\angle(\text{HC}_1\text{H}')^d = 116.3(7.2)^c$

<sup>a</sup> An experiment with CO<sub>2</sub> gave a correction of 0.1 % in the *s*-scale. The bond lengths are therefore 0.1 % longer than those directly determined by the least-squares refinements. The uncertainty in the *s*-scale (0.14 %) has been included in the standard deviations for bond distances. <sup>b</sup> The bond angles are those of the self-consistent  $r_\alpha$  structure. <sup>c</sup> These values are the results of a refinement where torsion angles,  $\angle\text{CCC}$ ,  $\angle\text{C}_2\text{CX}$ , and  $u$  values of non-bonded distances were not refined. <sup>d</sup> The projection of the angle  $\text{H}_1\text{C}_1\text{H}'_1$  in a plane perpendicular to the  $\text{C}_1-\text{C}_2$  axes (see Sect. V-A).

Parameter correlation,  $|\rho| > 0.49$ .  $\rho(\theta/\text{C}_2\text{CX}) = -0.57$ ,  $\rho[\theta/\phi_{1-2}(\text{AG})] = 0.83$ ,  $\rho[\theta/\phi_{2-3}(\text{AG})] = 0.68$ ,  $\rho(\theta/\phi(\text{GG})) = 0.94$ , and  $\theta = \angle\text{CCC}$ .

Table 11. Composition (at 65 °C) parameters ( $\alpha$ ) and torsion angles ( $a$ ) for 1,3-dibromopropane. Standard deviations are given in parenthesis.

Conformer	$\alpha(\%)$	$\phi_{1-2}(\text{deg.})$	$\phi_{2-3}(\text{deg.})$
GG	67(2)	113.4(2) <sup>b</sup>	113.4(2) <sup>b</sup>
AG	30(2)	119.2(6)	11.5(6)
AA	3(2) <sup>a</sup>	(-) <sup>c</sup>	(-) <sup>c</sup>

<sup>a</sup> The parameters  $\alpha(\text{GG})$  and  $\alpha(\text{AG})$  were refined with  $\alpha(\text{AA}) = 100\% - \alpha(\text{GG}) - \alpha(\text{AG})$ . <sup>b</sup>  $\phi_{1-2} = \phi_{2-3} = 120^\circ - \phi(\text{GG})$ ;  $\phi(\text{GG})$  was refined. <sup>c</sup>  $\phi_{1-2} = \phi_{2-3} = 0^\circ$ , see Fig. 1.

Parameter correlation,  $|\rho| > 0.49$ .  $\rho[\alpha(\text{AG})/\alpha(\text{GG})] = -0.73$ ,  $\rho[\phi_{1-2}(\text{AG})/\phi_{2-3}(\text{AG})] = 0.96$ ,  $\rho[\phi(\text{GG})/\phi_{1-2} \times \alpha(\text{AG})] = 0.79$ ,  $\rho[\phi(\text{GG})/\phi_{2-3}(\text{AG})] = 0.62$ .

Mean amplitudes of vibration ( $u$ ) from least-squares refinements and those determined by adjusting the torsional force constants (Sect. V-B) are compared in Table 12. The  $u$  values which are not found in Table 12 could not be refined as individual parameters, but their values have been adjusted in adjusting the torsional force constants as described in Sect.

V-B. Those  $u$  values and the corresponding  $K$  values are found in Table 8.

The mean amplitudes of the distances  $\text{X}\cdots\text{C}$  (g),  $\text{X}\cdots\text{X}(\text{AG})$  and in particular the amplitudes of the distances  $\text{X}\cdots\text{X}(\text{GG})$  are sensitive to the value of the torsional force constants. Keeping in mind the uncertainties, the refined and calculated  $u$  values generally agree.

Unfortunately the refined  $u$  values for  $\text{C}-\text{X}$ ,  $\text{C}_1\cdots\text{X}$  and  $\text{C}\cdots\text{X}(\text{gauche})$  are systematically lower than those calculated. This might indicate that the applied force constants ( $F(\text{CCX})$ ,  $F(\text{CCC})$ ,  $F(\text{C}-\text{C})$ ,  $F(\text{C}-\text{X})$ , and interaction constants among these) are not good enough. Comparison of frequencies in Table 7 lead to the conclusion that this is not the case.

The average relative deviation between the two sets of  $u$  values is ca. 10 %, while the average relative uncertainty of the refined  $u$  values is ca. 14 %.

In conclusion, the mean amplitudes calculated with the final torsional force constants seem the more reliable set of  $u$  values.

The final intensities and radial distribution curves are found in Fig. 3 and Fig. 4, respectively.

Cartesian coordinates for the conformers GG and AG together with the principal axes' moments of inertia are given in Table 13.

## VII. DISCUSSION

The percentage  $\alpha^*$  and  $\alpha$  of two conformers ( $\text{C}\equiv\text{C}^*$ ) in equilibrium in the gas phase, are related to the theoretical<sup>23</sup> expression<sup>24</sup> for the equilibrium constant, as given in eqn. (1):

$$\alpha^*/\alpha = (\text{M}^*/\text{M})(\text{Q}^*/\text{Q})^{\text{vib}} \exp(-\Delta E^{\text{m}}/RT) \quad (1)$$

with  $\text{M}^*/\text{M} = (\text{M}_d^*/\text{M}_d)(\sigma^*/\sigma)^{-1} = \text{M}_c^*/\text{M}_c$  (see Table 1)

(The classical rotational partition functions of the conformers are approximately equal.)  $\text{Q}^{\text{vib}}$  is the vibrational partition function of a conformer referred to the potential-energy minimum of that conformer.  $\Delta E^{\text{m}} = E^* - E$  is the potential-energy difference between the conformer C and C\*, and the difference is measured between energy minima. The zero-point vibrational energy is included in the quantity  $\text{Q}^{\text{vib}}$ .  $R$  and  $T$  have their usual thermodynamic meanings.

If the vibrational partition functions are

Table 12. Mean amplitudes of vibration ( $u$ ) for 1,3-dibromopropane at 65 °C.

Distance type	Dist. (Å)	Refined $u$ -value (Å)	Standard deviation	Calculated <sup>a</sup> $u$ -value (Å)
C-H	(1.11)	0.080	0.011	0.078-9
C-C	(1.52)	0.051	0.008	0.051
C-X	(1.95)	0.041	0.006	0.055
C <sub>2</sub> ...X	(2.88)	0.063	0.007	0.076
X <sub>1</sub> ...H <sub>1</sub>	(2.49)	0.109	0.013	0.113
X...X(GG)	(4.41)	0.279	0.010	0.268
X...C(g) in GG	(3.33)	0.124 <sup>b</sup>	0.052	0.158
X...X(AG)	(5.13)	0.145	0.020	0.166
X...C(g) in AG	(3.33)	0.129 <sup>b</sup>	0.052	0.161

<sup>a</sup> The valence force constants are found in Table 6. <sup>b</sup> refined as one parameter.

Parameter correlation,  $|\rho| > 0.49$ .  $\rho[\text{CC}_2\text{H}/u(\text{C}_1\cdots\text{X}_1)] = 0.63$ ,  $\rho[\text{CCX}/u(\text{X}_1\cdots\text{H}_1)] = 0.65$ ,  $\rho(\text{CC}_2\text{H}/u(\text{X}_1\cdots\text{H}_1)) = -0.76$ ,  $\rho[\alpha(\text{AG})/u(\text{AG})] = 0.59$ ,  $\rho[\text{SCALE}/u(\text{GG})] = 0.55$ , with  $u(\text{AG})$  and  $u(\text{GG})$  representing the  $u$  values of the X...X distances.

Table 13. Cartesian coordinates (Å) for conformers of 1,3-dibromopropane. The coordinates have been calculated using the final  $\angle_\alpha$  values for angles and  $r_g (r_g = r_a + u^2/r)$  values (C-H: 1.132 Å, C-C: 1.529 Å, C-Br: 1.961 Å) for the bond lengths. The numbering of atoms in the conformer GG is shown in Fig. 2. The principal axes' moment of inertia ( $\text{amu Å}^2$ ) are:

$I_A = 100.7$ ,  $I_B = 843.0$ ,  $I_C = 877.4$  for GG  
 $I_A = 65.0$ ,  $I_B = 1111.8$ ,  $I_C = 1157.2$  for AG  
 $I_A = 41.1$ ,  $I_B = 1390.5$ ,  $I_C = 1142.2$  for AA

Conformer GG:			Atom	Conformer AG		
(x)	(y)	(z)		(x)	(y)	(z)
1.2627	0.8617	0.0000	C <sub>1</sub>	1.2627	0.8617	0.0000
1.4638	1.8721	-1.6684	Br <sub>1</sub>	1.3709	2.0083	-1.5870
2.2333	0.2998	0.1509	H <sub>1</sub>	2.2389	0.2915	0.0479
1.3347	1.6166	0.8399	H <sub>1</sub> '	1.3842	1.5440	0.8945
0.0000	0.0000	0.0000	C <sub>2</sub>	0.0000	0.0000	0.0000
0.0000	-0.4510	1.0378	H <sub>2</sub>	0.0000	-0.4510	1.0378
0.0000	-0.4510	-1.0378	H <sub>2</sub> '	0.0000	-0.4510	-1.0378
-1.2627	0.8617	0.0000	C <sub>3</sub>	-1.2627	0.8617	0.0000
-1.4638	1.8721	1.6684	Br <sub>3</sub>	-2.8743	-0.1947	0.3623
-2.2333	0.2998	-0.1509	H <sub>3</sub>	-1.4627	1.4289	-0.9585
-1.3347	1.6166	-0.8399	H <sub>3</sub> '	-1.2676	1.7149	0.7433

known, then the quantity  $\Delta E^m$  may be computed from eqn. (1). Conversely, if the quantity  $\Delta E^m$  is known, then the ratio between  $Q^{\text{vib}}$  values may be calculated from eqn. (1).

According to the semiempirical energy model, AA is the conformer of lowest minimum energy, while the conformers GG and AG are 0.89 and 0.38 kcal/mol less stable than AA, respectively. If these values of  $\Delta E^m$  are accepted, then the ratios ( $q$ ) between the vibrational partition functions of the conformers have to be quite different from 1.0, as shown in Table 14 (I). On the other hand, if the conformers have equal vibrational partition functions ( $q=1$ ) the  $\Delta E^m$

values of Table 14 (II) show that GG is the most stable conformer.

In order to explain the experimental composition (Table 11) two possibilities have to be considered: (I) the conformational energies ( $\Delta E^m$ ) predicted by the semiempirical calculations are approximately correct, but the conformer GG has a much lower zero-point vibrational energy ( $q \gg 1$ ) than AG and AA; (II) the conformers have approximately equal zero-point vibrational energies ( $q=1$ ), but then the  $\Delta E^m$  values of the conformers have to be quite different from those calculated from the semiempirical energy model.

Table 14. Energy differences,  $\Delta E^m$  (kcal/mol), and ratios ( $q$ ) between vibrational partition functions of the conformers  $GG$ ,  $AG$ , and  $AA$  of 1,3-dibromopropane at 65 °C.

Difference or ratio	$GG/AG$	$GG/AA$	$AG/AA$
$\Delta E^m$ (CALC.) <sup>a</sup> , see Table 3	+0.51	+0.89	+0.38
(I) Ratio ( $q$ ) <sup>b</sup> between vibrational partition functions if $\Delta E^m$ (CALC.) values are used	9.45	24.1	3.96
(II) $\Delta E^m$ values <sup>c</sup> if $q=1$	-0.94	-1.62	-0.62

<sup>a</sup>  $\Delta E^m$  (CALC.) are the conformational-energy differences (between energy minima) predicted by the semiempirical calculations. <sup>b</sup>  $q=(Q^*/Q)^{vib}$ , calculated according to eqn. (1). <sup>c</sup> Calculated according to eqn. (1). The nozzle temperature (65 °C) and the composition parameters of Table 11 were used.

The conformational force fields have to be very different for the first (I) possibility to be correct. Is there any additional experimental evidence that can support this point? Most probably, the conformational differences in force fields are due to different torsional force constants. A complete set of experimental frequencies for each conformer does not exist, therefore vibrational spectroscopy can not, at present, prove or disprove the first possibility. If the torsional force constant of  $GG$  [ $F_\phi = 0.243$  mdyn Å (rad)<sup>-2</sup>] is accepted, then the average value ( $\bar{F}_\phi$ ) of  $AG$  had to be unreasonably large to yield a  $q$  value ( $GG/AG$ ) of 9.45. With  $F_\phi(GG) = 0.243$  and  $\bar{F}_\phi(AG) = 0.480$  the  $q$  value is 5.48 as shown in Table 9. The values of  $q(GG/AA)$  and  $q(AG/AA)$  critically depend on the value of the composition parameter  $\alpha(AA)$ . In conclusion, the first possibility seems unlikely, but the second possibility is not thereby proved. The correct  $\Delta E^m$  values are probably a compromise between the two sets (I and II in Table 14).

The torsional frequencies reported for the conformer  $GG$  ( $\omega_1 = 176$  and  $\omega_2 = 186$  cm<sup>-1</sup>) in Ref. 7 are not consistent with those derived from the electron diffraction data:  $\omega_1 = 47 \pm 10$  cm<sup>-1</sup> and  $\omega_2 = 149 \pm 15$  cm<sup>-1</sup>. The error limits here correspond to the error limits of the torsional force constant (Sect. V-B). Although the spectroscopic values (liquid) ought to be somewhat larger than those from electron diffraction (gas), the shift could not be that great. In conclusion,

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the lowest frequency ( $\omega_1$ ) has not been detected.<sup>7</sup> This was also the conclusion in the case of 1,2,3-tribromopropane.<sup>8</sup> The spectroscopic value of  $\omega_2$  is not excluded, since a shift in going from gas to liquid is possible.

The difference  $\Delta\omega_{43} = \omega_4 - \omega_3$  according to the present normal-coordinate analysis is 182 cm<sup>-1</sup>, but the observed difference is only 14 cm<sup>-1</sup>. The force field in Table 6 would have to be changed drastically in order to account for this observation. On the other hand, the assignment of  $\omega_3$  could be wrong. Moreover, the large discrepancies would be removed if the assignment were changed as follows:  $\omega_1$  (not observed),  $\omega_2 = 176$  and  $\omega_3 = 186$  cm<sup>-1</sup>. The value of 310 cm<sup>-1</sup> for  $\omega_3$  then must be given a new interpretation.

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## REFERENCES

1. Sheppard, N. *J. Mol. Struct.* 6 (1970) 5.
2. Bastiansen, O., Seip, H. M. and Boggs, J. E. In Dunitz, J. D. and Ibers, J. A., Eds.,

- Perspectives in Structural Chemistry*, Wiley, New York 1971, Vol. IV.
3. 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.
  4. Bartell, L. S. *Private communication*.
  5. Brown, J. K. and Sheppard, N. *Proc. Roy. Soc. (London) A* 231 (1955) 555.
  6. Dempster, A. B., Price, K. and Sheppard, N. *Spectrochim. Acta Part A* 25 (1969) 1381.
  7. Thorbjørnsrud, J., Ellestad, O. H., Klæboe, P. and Torgrimsen, T. *J. Mol. Struct.* 15 (1973) 61.
  8. Stølevik, R. *Acta Chem. Scand. A* 28 (1974) 299.
  9. Abraham, R. J. and Parry, K. J. *J. Chem. Soc. B* (1970) 539.
  10. Schachtschneider, 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.
  11. Snyder, R. G. *J. Mol. Spectrosc.* 28 (1960) 273.
  12. Gwinn, W. D. *J. Chem. Phys.* 55 (1971) 477.
  13. Stølevik, R., Seip, H. M. and Cyvin, S. J. *Chem. Phys. Lett.* 15 (1972) 263.
  14. Zeil, W., Haase, J. and Wegmann, L. *Z. Instrumentenk.* 74 (1966) 84.
  15. Bastiansen, O., Graber, R. and Wegmann, L. *Balzer's High Vacuum Report* 25 (1969) p. 1.
  16. Andersen, B., Seip, H. M., Strand, T. G. and Stølevik, R. *Acta Chem. Scand.* 23 (1969) 3224.
  17. Peacher, J. and Willis, J. C. *J. Chem. Phys.* 46 (1967) 4809.
  18. Strand, T. G. and Bonham, R. A. *J. Chem. Phys.* 40 (1964) 1686.
  19. Almenningen, A., Bastiansen, O. and Munthe-Kaas, T. *Acta Chem. Scand.* 10 (1956) 261.
  20. Morino, Y., Kuchitsu, K. and Oka, T. *J. Chem. Phys.* 36 (1962) 1108.
  21. Kuchitsu, K. *J. Chem. Phys.* 49 (1968) 4456.
  22. Seip, H. M. and Stølevik, R. In Cyvin, S. J., Ed., *Molecular Structures and Vibrations*, Elsevier, Amsterdam 1972, p. 171.
  23. Glasstone, S. *Theoretical Chemistry*, Van Nostrand, New York 1944.
  24. Herzberg, G. *Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand, Princeton, N. J. 1945.

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