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Conformational Analysis. XI. The Molecular Structure, Torsional Oscillations, and Conformational Equilibria of Gaseous Tetrakis-(bromomethyl)methane, $C(CH_2Br)_4$, as Determined by Electron Diffraction and Compared with Molecular-Mechanics Calculations

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Gaseous $C(CH_2Br)_4$ has been studied by electron diffraction. Two conformers named *D* (D_{2d} symmetry) and *S* (S_4 symmetry) were detected. The results are presented with error limits (2σ). The following values for distances (r_g) and angles ($\angle_\alpha$) are appropriate for the structure of both conformers: $r(C-H) = 1.09(5)$ Å, $r(C-C) = 1.554(9)$ Å, $r(C-Br) = 1.951(8)$ Å, $\angle CCBr = 114.2°(0.8)$, $\angle CCH = 111.7°(3.2)$. *D* and *S* have a tetrahedral arrangement of carbon atoms and all-staggered (1:2) conformations which do not possess parallel (1:3) Br···Br interactions. Torsional force constants and vibrational frequencies for both conformers have been estimated. The composition at 140 °C is 42(2) % of *S* and 58(2) % of *D*. As predicted by the molecular-mechanics calculations, conformers possessing parallel (1:3) Br···Br interactions are not present in detectable amounts. To a large extent the structural parameters obtained by the molecular-mechanics calculations reasonably agree with the experimental results.

I. INTRODUCTION

This work is part of a systematic conformational study of halogenated propanes and related molecules by electron diffraction in the gas phase. Results for the following molecules have been published: $[CH_2Br-CHBr-CH_2Br]$,[1] $[C(CH_2Cl)_4]$,[2] $[(CH_3)_2C(CH_2Cl)_2]$,[3] $[CH_3-C(CH_2Cl)_3]$,[4] $[CH_2Br-CH_2-CH_2Br]$,[5] $[CH_2Cl-CHCl-CH_2Cl]$,[6] $[CCl_3-CCl_2-CCl_3]$,[9] $[CCl_3-CCl_2-CHCl_2]$,[6] $[CCl_3-CH_2-CHCl_2]$,[8] $[CHCl_2-CCl_2-CHCl_2]$.[10]

$C(CH_2X)_4$(X = F, Cl, Br, I) compounds will be referred to in general as TMX. The number of possible staggered conformers in TMX is 81, but only six are spectroscopically distinguishable.[2] All conformers, except two, have one or more parallel (1:3) X···X interactions. The two exceptions are shown in Fig. 1, and these conformers will be referred to as **D** (possessing D_{2d} symmetry) and **S** (possessing S_4 symmetry), respectively.

$TMCl$[2] has been studied by electron diffraction. Only two conformers (**D** and **S**) were detected. **D** and **S** are present in *equal* amounts at a temperature of 105 °C. References to structural work on TMBr, spectroscopic studies, and measurements of dipole moments, are found in Ref. 2. However, the conformational equilibria of TMBr were not quantitatively described before the present work.

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

The semi-empirical energy model corresponds to molecular-mechanics calculations, including atom-atom potentials and valence force constants as described in Ref. 1. Energy parameters were taken from the work of Abraham and Parry,[11] and the valence force constants in Table 4 were used. The "normal" values of the geometry parameters are given in Table 1. In minimizing the energy, the geometry was constrained in the same way as described in Sect. V-A, except that all torsion angles were ad-

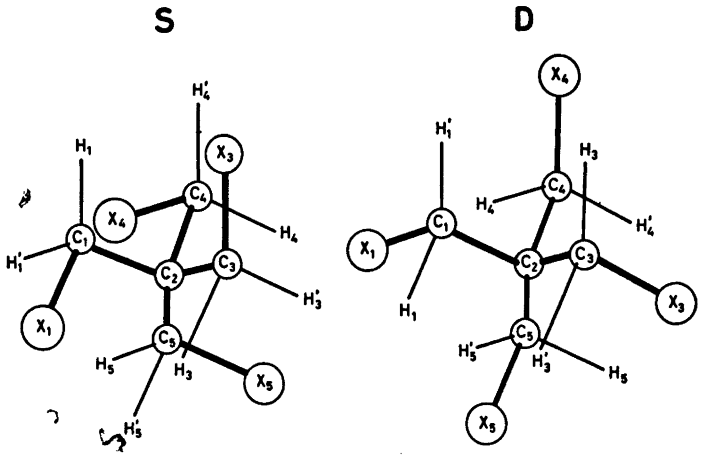

Fig. 1. Numbering of atoms in the two conformers **D** and **S** of $C(CH_2X)_4$. The conformer **D** has D_{2d} symmetry: three C_2 (mutually perpendicular), one S_4 (coincident with one C_2), two σ_d (through S_4). The **S** conformer has S_4 symmetry: one S_4 coincident with one C_2.

justed as independent variables. The conformational geometries derived from the semi-empirical energy model are present in Table 1. Calculated structure parameters indicate small deviations from staggered geometry in the conformer **S**, while there are no such deviations indicated for conformer **D**. Moreover, small deviations from a tetrahedral carbon framework are indicated for both **D** and **S**. The same indications were observed for TMCl.[3]

According to the present energy model, conformer **S** is 0.51 kcal/mol (Table 2) more stable than conformer **D**, while the corresponding value for TMCl [3] is 0.75 kcal/mol.

The conformers with *one* parallel (1:3) X···X interaction have their torsion angles displaced from staggered values. The energy of these conformers is thereby considerably lowered. However, the lowest energy obtained by minimalization was still more than 5 kcal/mol higher than the value for the conformer **D**. The calculations also lead to the conclusion that the *eclipsed* conformer of lowest energy is about 5 kcal/mol less stable than conformer **D**.

Some of the torsional barriers have to be high, and probably all of them are too high to be detected by electron diffraction. Nevertheless, NMR studies might lead to some information. Therefore, it is of interest to estimmate the value of the *lowest* barrier height when a conformation **S** is changed into **D** by rotations of $-CH_2X$ groups around the C–C

Table 1. Calculated geometries for the conformers **D** and **S** of $C(CH_2Br)_4$.

Type of parameter	"Normal" value	D	S
C–H (Å)	1.094	1.093	1.093
C–C (Å)	1.513	1.537	1.536
C–X (Å)	1.935	1.945	1.945
$C_1C_2C_3$ (°)	109.47	107.7	110.9
CCX (°)	109.47	113.0	112.9
CCH (°)	109.47	110.1	110.1
ϕ_{1-2} (°)	(−)[a]	0.0[b]	+123.5[c]
ϕ_{2-2} (°)	(−)	0.0	+123.5
ϕ_{4-2} (°)	(−)	0.0	−123.5
ϕ_{5-2} (°)	(−)	0.0	−123.5

[a] Torsion angles were adjusted as four independent variables for each conformer. [b] No deviation from staggered values. [c] Staggered values $|\phi| = 120°$.

Table 2. Calculated conformational energies (in kcal/mol) in $C(CH_2Br)_4$.

Type of energy	D	S
E (bonded)	2.70	2.58
E (van der Waals)	2.22	2.17
E (polar: X···H)	−15.50	−15.66
E (polar: X···X)	8.66	8.48
E (total)	−1.92	−2.43

bonds. If high barriers are to be avoided, then conformational minima, corresponding to conformers of low symmetry (C_1), are always reached before **S** is changed into **D** by rotations around C–C bonds. The conformers **S** and **D** are thus separated by double-maxima as indicated below:

S(0)→MAX(10.7)→C_1(5.6)→MAX(10.7)→**D**(0.5)

The energy values (kcal/mol) relative to the conformer **S** are shown in parentheses. The corresponding values for TMCl [2] are:

0→18→6→18→0.8.

Valence force constants were *numerically* computed from the energy model. Torsional force constants are given in Table 3.

III. CALCULATION OF VIBRATIONAL QUANTITIES

Valence force constants, except for the torsional part, were taken from the works of Schachtschneider [12] and Snyder.[13] The final force constant values used are shown in Table 4.

The normal coordinate program described by Gwinn [14] was used in computing vibrational frequencies.

Table 3. Calculated torsional force constants (in mdyn Å(rad)²) for conformers of $C(CH_2Br)_4$.

	D	**S**
F_ϕ (diagonal)[a]	0.26	0.25
$F_{\phi\phi'}$ (AA)[b]	−0.012	–
$F_{\phi\phi'}$ (AG)[b]	–	−0.040
$F_{\phi\phi'}$ (GG)[b]	−0.048	−0.032
$F(++++)$[c]	0.62	0.57
$F(++--)$[c]	1.38	1.21
$F(+-00)$[c]	0.54[d]	–
$F(+-+-)$[c]	–	1.13[d]

[a] $F_\phi(1\text{-}2)=F_\phi(3\text{-}2)=F_\phi(4\text{-}2)=F_\phi(5\text{-}2)=F_\phi$. [b] In the conformer **D** are two different kinds of $F_{\phi\phi'}$, interaction constants (AA and GG) corresponding to XCCCX fragments having their X···X distances AA or GG, respectively; in the **S** conformer are constants of type AG as well as GG. [c] $F(++++)$, $F(++--)$, $F(+-00)$, and $F(+-+-)$ are second order derivatives of the energy with respect to ϕ, under the constraints of the torsional modes approximately), as follows:

$(++++)$; $\Delta\phi_{3-2}=\Delta\phi_{3-2}=\Delta\phi_{4-2}=\Delta\phi_{5-2}=\Delta\phi$
$(++--)$; $\Delta\phi_{1-2}=\Delta\phi_{3-2}=\Delta\phi$ and $\Delta\phi_{4-2}=\Delta\phi_{5-2}=-\Delta\phi$
$(+-00)$; $\Delta\phi_{1-2}=\Delta\phi_{3-2}=\Delta\phi$ and $\Delta\phi_{4-2}=\Delta\phi_{5-2}=0$
$(+-+-)$; $\Delta\phi_{1-2}=\Delta\phi_{4-2}=\Delta\phi$ and $\Delta\phi_{3-2}=\Delta\phi_{5-2}=-\Delta\phi$

[d] Degenerate mode belonging to species E.

Table 4. Valence force constants for $C(CH_2Br)_4$.

Stretch (mdyn/Å)
C–C = 4.534
C–H = 4.850
C–X = 2.630
HCH = 0.500
HCX = 0.690
CCH = 0.670

Bend (mdyn Å/rad)²)
CCX = 0.910
CCC = 1.086

Stretch/stretch (mdyn/Å)
(C common): C–C/C–X = 0.35, C–C/C–C = 0.101, C–H/C–H = −0.007
Stretch/bend (mdyn/rad)
(C–C common): C–C/CCC = 0.417, C–C/CCX = 0.030, C–C/CCH = 0.260
(C–X common): C–X/HCX = 0.26, C–X/CCX = 0.49
Bend/bend (combination of two angles with the central C atom common, mdyn Å/(rad)²)
(C–X common): HCX/HCX = 0.05, (C–H common): HCC/HCX = 0.074
(C–C common): HCC/HCC = −0.026, (C common): HCC/HCX = 0.029
Bend/bend (combination of two angles with C–C common and dihedral angle *anti* or *gauche*)
anti: CCC/CCX = 0.093, HCC/CCC = 0.072
gauche: CCC/CCX = −0.024, HCC/CCC = −0.058
Torsion (mdyn Å/(rad)²), see also Sect. V-B
$F_\phi(S)_v = 0.86$; for conformer *S*
$F_\phi(D)^a = 0.33$; for conformer *D*

[a] The torsional force constants have been defined in the following way: each fragment A–C–C–C (A = H, X see Fig. 1) has been assigned an equal torsional force constant. The total force constant for the torsional coordinate ϕ_{i-2} (i = 1,3,4,5) is thus the sum of *nine* equal contributions, one from each fragment $A-C_i-C_2-C$.

Table 5. Calculated u and (K) values (Å) for internuclear distances in $C(CH_2Br)_4$ at 140 °C. The valence force field given in Table 4 was used.

Distance type	r (Å)	$F_\phi = 0.33$	$F_\phi = 0.55$	$F_\phi = 0.86$
C–H	1.077	0.078(0.0235)	0.078(0.0201)	0.078(0.0180)
C–C	1.544	0.052(0.0052)	0.052(0.0047)	0.052(0.0043)
C–X	1.942	0.057(0.0188)	0.057(0.0143)	0.057(0.0116)
$C_1 \cdots C_3$	2.52	0.077(0.0048)	0.076(0.0041)	0.074(0.0036)
$C_1 \cdots C_4$	2.52	0.077(0.0056)	0.076(0.0051)	0.075(0.0047)
C···X	2.95	0.081(0.0137)	0.080(0.0107)	0.080(0.0088)
C···H	2.13	0.111(0.0157)	0.110(0.0133)	0.110(0.0118)
X···H	2.49	0.114(0.0282)	0.113(0.0212)	0.112(0.0172)
H···H	1.78	0.125(0.0318)	0.124(0.0260)	0.124(0.0226)
X···X(GG)	4.17	0.284(0.0100)	0.242(0.0086)	0.213(0.0077)
X···X(AG)	5.11	0.187(0.0087)	0.175(0.0066)	0.167(0.0053)
X···X(AA)	5.89	0.113(0.0065)	0.112(0.0046)	0.112(0.0035)
C···X(g)	3.31	0.164(0.0112)	0.153(0.0089)	0.145(0.0075)
C···X(a)	4.32	0.079(0.0087)	0.078(0.0067)	0.078(0.0055)
X···H(GG)	2.79	0.254(0.0198)	0.238(0.0156)	0.227(0.0131)
X···H(AG)	4.27	0.184(0.0138)	0.174(0.0113)	0.168(0.0098)
X···H(AG)	4.55	0.166(0.0127)	0.160(0.0098)	0.156(0.0081)
X···H(GG)	3.63	0.242(0.0144)	0.214(0.0120)	0.195(0.0106)
X···H(AA)	5.07	0.128(0.0120)	0.128(0.0095)	0.127(0.0079)
C···H(g)	2.71	0.160(0.0121)	0.154(0.0100)	0.149(0.0087)
C···H(a)	3.44	0.106(0.0123)	0.106(0.0108)	0.106(0.0097)

Mean amplitudes of vibration corresponding to three different values of the torsional force constants were calculated as described in Ref. 15. In Table 5 are given u and K values [15] for internuclear distances. Some of these quantities are quite sensitive to the values of torsional force constants, which have been adjusted to fit the experimental intensities, as described in Sect. V-B.

Several other vibrational quantities in a molecule like TMBr also vary with the torsional force constants. To illustrate this point, some of these quantities have been calculated using different values of the torsional force constants, and the results are found in Tables 6 and 7.

The best estimates of the torsional force constants (see Sect. V-B) are 0.33 and 0.86 mdyn Å(rad)$^{-2}$ for the conformers **D** and **S**, respectively. Calculated frequencies corresponding to force constants within this range have been shown in Table 6. Frequency values in the range 40 – 60 cm^{-1} have to be expected for the conformers **D** and **S**. Generally the lowest frequency values correspond to torsional oscillations, however, bending frequencies down to *ca.* 50 cm^{-1} have to be expected for both con-

Table 6. Calculated frequencies in the range 40 – 335 cm^{-1} for conformers of $C(CH_2Br)_4$. Frequencies corresponding to torsional oscillations are indicated by (ϕ), and degenerate frequencies (species E) by *d*.

$F_\phi = 0.33$		$F_\phi = 0.55$		$F_\phi = 0.86$	
D	**S**	**D**	**S**	**D**	**S**
40(ϕ)	41(ϕ)	47(ϕ)	49(ϕ)	54.1(ϕ)	55
52(ϕ)[a]	49(ϕ)	54	53	54.3	56(ϕ)
53	56	62(ϕ)[d]	63(ϕ)	71(ϕ)[d]	71(ϕ)
110	73(ϕ)[d]	111	80(ϕ)[d]	113	85(ϕ)[d]
178	137	178	137	179	138
191[d]	192[d]	200[d]	219[d]	211[d]	245[d]
220(ϕ)	291	234	303	239	316
231	295	276(ϕ)	312	335(ϕ)	328

Table 7. Ratios ($q = Q_D/Q_S$) between vibrational partition functions (Q) for conformers of $C(CH_2Br)_4$ at 140 °C. Q is referred to the conformational energy minimum, and F_ϕ is the torsional force constant in mdyn Å (rad)$^{-2}$.

F_ϕ(S)	F_ϕ(D)	0.33	0.55	0.86
0.33		1.054	0.156	0.019
0.55		7.107	1.054	0.127
0.86		58.83	8.724	1.054

formers. Clearly some of the vibrational modes correspond to a rather complicated mixture of bending as well as torsional motion.

In order to calculate the conformational energy difference an estimate of the vibrational partition functions (Q) of the conformers are needed (Sect. VII). The ratio (q) between Q-values varies dramatically with the value of the torsional force constant as shown in Table 7. The difference in zeropoint vibrational energy is included in these ratios.

IV. EXPERIMENTAL AND DATA REDUCTION

TMBr was obtained from FLUKA. After recrystallization from CH_3CH_2OH and sublimation of the crystals, the sample melted at 162 – 163 °C.

Electron diffraction photographs were made at a nozzle temperature of 140 °C in the Oslo apparatus [16] under the following conditions.

Nozzle-to-plate, distance (mm)	480.78	481.22	201.22
Electron wavelength (Å)	0.06460	0.06458	0.06458
Number of plates	6	5	5
Range of data, in s(Å^{-1})	1.50– 19.125	1.375– 19.125	7.00– 43.00
Data interval, Δs(Å^{-1})	0.125	0.125	0.25
Estimated uncertainty in the s-scale (%)	0.14	0.14	0.14
Sector-to-plate distance (mm)	14.12	15.30	15.30

The electron wavelength was determined by calibration against gold, and corrected by an experiment with CO_2 giving a correction of +0.1 % in the s-scale. The data were reduced in the usual way to yield an intensity curve for *each plate*. Average curves for each set of distances were formed. The two 48 cm curves were then averaged. A composite curve was made by connecting the 48 cm and 20 cm average curves after scaling. The final experimental intensity curve is shown in Fig. 2. The intensities have been modified by $s/|f_{Br}'|^2$. The scattering amplitudes were calculated by the partial wave method [18] using Hartree-Fock atomic potentials.[19]

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

The radial distribution curve obtained by Fourier transformation of the final experimental intensity is presented in Fig. 3.

For the final least-squares refinements data from $s = 1.50$ Å^{-1} to $s = 23.50$ Å^{-1} were used. The data beyond this range were of lower quality.

V. STRUCTURE ANALYSIS AND REFINEMENTS

The calculated conformational energies suggest that only two conformers, **D** and **S**, are present in detectable amounts at 140 °C. From the areas under the two peaks (see Fig. 3) corresponding to the distances X···X(AG) and X···X(AA) it was easily concluded that **D** and **S** have to be present in nearly equal amounts.

A. Least-squares refinements. The least-squares program is a modified version of the program explained in Ref. 17. Several conformers may be included in the refinements with the present version of the program.

Models for the conformers were constructed with the following geometrical assumptions: (1) the C-atom framework possess D_{2d} symmetry, with $\angle C_1C_2C_3 = \angle C_4C_2C_5 = 109.47° - \theta_C$ for the **D** conformer and $\angle C_1C_2C_3 = \angle C_4C_2C_5 = 109.47° + \theta_C$ for the **S** conformer; (2) all four $C-CH_2X$ groups are equal; (3) each of the $C\text{-}CH_2X$ groups possess C_s symmetry, and the projection of the angle HCH′ on a plane perpendicular to the C – C axis is 120°; (4) the conformers **D** and **S** have identical structures except for the C – C torsion angles and the CCC angles.

Models were defined in terms of the following average parameters: C – H, C – C, C – X, ∠CCX, ∠CCH and θ_C. The torsion angles of the **S** conformer were defined as follows: $\phi_{1-2} = \phi_{3-2} = 120° + \phi_s$ and $\phi_{4-2} = \phi_{5-2} = -120° - \phi_s$. The deviation angle ϕ_s was refined. All torsion angles for the **D** conformer are equal to 0°. The exact staggered conformers thus have

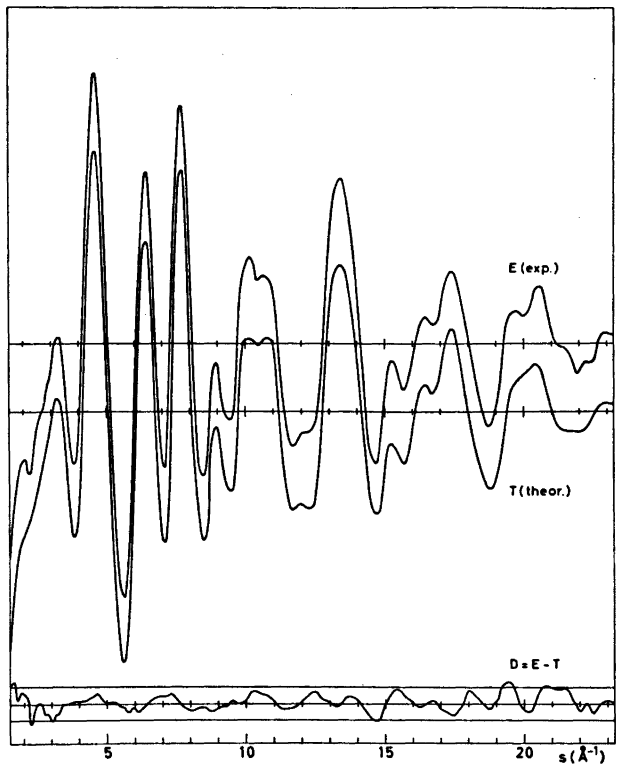

Fig. 2. Intensity curves for $C(CH_2Br)_4$ at 140 °C. Curve E shows the experimental intensity, and curve T the theoretical intensity corresponding to the final least-squares parameters. Curve D is the experimental minus theoretical, and the straight lines give the experimental uncertainty ($\pm 3 \times$ experimental standard deviation).

torsion angles: 120, 120, −120, −120° for **S** and 0, 0, 0, 0° for **D**.

Also adjusted was the composition parameter, the relative amount of conformer **S**.

In the first part of the structure analysis a number of refinements were carried out, in which selected combinations of parameters were allowed to vary, while others were held constant at plausible values. At some stages the background had to be corrected, however, none of the important conclusions about the structure and composition were changed thereby.

All important parameters could be simultaneously refined. The combination of all geometry variables, the u values for bond distances and for non-bonded distances of the kinds C···C, X···X and X···C, the composition parameter, and a scale factor refined to give convergence.

B. Determination of torsional force constants. The torsional modes of vibration contribute substantially to the mean amplitudes of several distances. Therefore, since a reasonable force field is known, except for the torsional part, the torsional force constants can be adjusted to fit the electron-diffraction data. The procedure used for TMCl [2] was used in order to estimate the diagonal torsional force constants of the conformers of TMBr. The most probable torsional force constants, as determined from the electron-diffraction data, are:

For **D**: $F_\phi = 0.33(-0.05, +0.15)$ mdyn Å(rad)$^{-2}$

For **S**: $F_\phi = 0.86(-0.25, +0.10)$ mdyn Å(rad)$^{-2}$

The error limits are subjective to a certain degree. Not all combinations of F_ϕ values are equally probable. Combinations of values [F_ϕ(D), F_ϕ(S)] within a triangle having corners

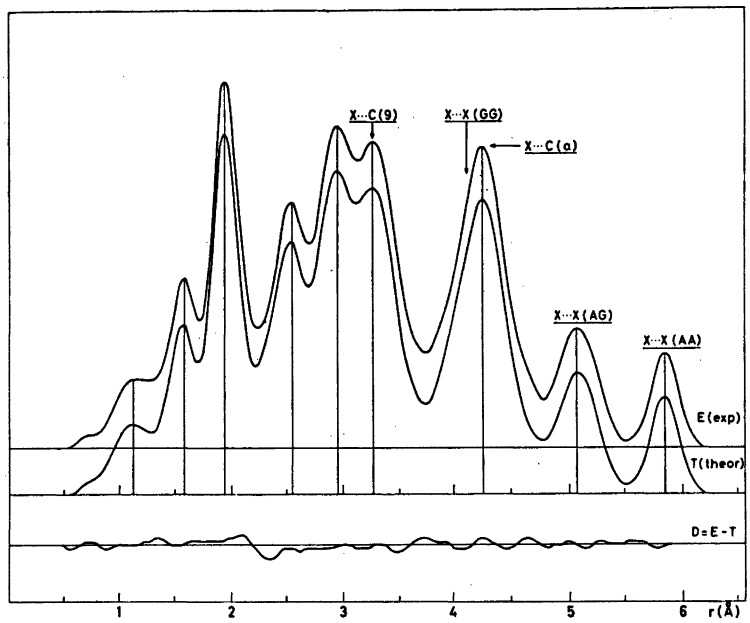

Fig. 3. Radial distributions for $C(CH_2Br)_4$ at 140 °C. Experimental (E) and theoretical (T) radial distribution curves and difference curve (D). The RD curves were calculated from the intensity curves of Fig. 2 with an artificial damping constant 0.0020 Å^2.

[0.27, 0.94], [0.34, 0.94], and [0.40, 0.61] are very probable. Error limits as indicated here do not allow for *systematic* errors in the remainder of the force field, nor in the temperature. These points have been discussed in a previous paper.[7]

VI. FINAL RESULTS

Results from the least-squares refinements, and standard deviations (σ) corrected for correlation in the experimental data,[20] are given. All intensities were given equal weights in the final refinements.

Non-bonded distances were restricted under the geometrical constraint of r_α parameters, by including correction terms $D=r_\alpha-r_a$ ($D=(u^2/r)-K$) for all distances.[21,22] Calculated u and K values, corresponding to final torsional force constants, are shown in Table 5. Structure parameters are given in Table 8. The uncertainty in the s-scale (0.14 %) has been included in the σ values. An experiment with CO_2 gave a correction of +0.1 % in the s-scale, therefore the bond lengths in Table 8 are 0.1 % longer than those obtained directly by refinements. The values of the deviation parameters, θ_c and θ_s, are not significantly different from zero.

The relative amounts of the conformers **D** and **S** were determined by refining the composition parameter α(S) with the restriction that $\alpha(S)+\alpha(D)=100$. The best least-squares estimate was $\alpha(S)=42$ % with $\sigma=1$ %.

Several u values have been refined and compared to those computed using the final torsional force constants. (see Table 9) Both sets of u values are experimental, but the calculated values combine information from spectroscopy as well as from electron diffraction. Some u values get very small contributions from the torsional modes of vibration. Such u valuès are those corresponding to bond distances, distances over *one* bond angle, the distances X···X(AA), and the distance X···C(a). The fact that these u values are generally in good agreement with those refined directly, is important. The force field used for TMBr thus seems reasonable. The value of u(C−X), determined directly by least-squares refinements,

Table 8. Structure parameters for $C(CH_2Br)_4$.

Bond lengths (Å)	r_a	σ
C–H	1.082	0.024
C–C	1.552	0.005
C–Br	1.949	0.004
Bond angles (°)	$\angle_\alpha$	σ
CCBr	114.2	0.4
CCH	111.7	1.6
CCC	(109.5)[a]	(0.9)[a]
HCBr	105.8[b]	1.6
Torsional deviation	ϕ_s (°)	σ (°)
angle in conformer **S**	+0.1[c]	0.8

[a] $\theta_c = +0.8°$ $\sigma(\theta_c) = 0.9°$, see Sect. V–A. [b] Dependent parameter. [c] See Sect. V–A for definition.

is significantly different from the spectroscopic value, probably due to an error in blackness correction. It is, however, unlikely that other u values are significantly disturbed by this type of error. The average deviation between the two sets of u values, $\langle|\Delta|/u\rangle$, is ca 17 %, while the average relative uncertainty, $\langle\sigma/u\rangle$, of the refined u values is ca 20 %. If only torsion dependent u values are included then $\langle|\Delta|/u\rangle = 10$ % and $\langle\sigma/u\rangle = 15$ %. In conclusion, the vibrationally consistent set of u and K values in Table 5 are considered the final ones for TMBr.

Parameter correlation coefficients (ϱ) with absolute values larger than 0.5 were obtained for the following parameter combinations:

Combination	ϱ-Value
CCX/C–X	−0.52
θ_c/CCX	−0.60
θ_c/ϕ_s	−0.84
u[X···C(a)]/u[X···C(g)]	−0.95
α(S)/u[X···X(AG)]	+0.60
scale/u(C–X)	+0.54

VII. DISCUSSION

The percentages α(D) and α(S) of the two conformers are related to the expression for the equilibrium constant as given in eqn. (1)

$$\alpha(D)/\alpha(S) = \tfrac{1}{2}(Q_D/Q_S)^{vib}\exp(-\Delta E^m RT) \quad (1)$$

(The *classical* rotational partition functions for the two conformers are very nearly equal.) Q^{vib} is the vibrational partition function, referred to the *minimum* of potential energy, for a conformer. $\Delta E^m = E_D{}^m - E_S{}^m$ is the difference in potential energy between the two conformers, and the difference is measured between energy *minima*. The difference in zero-point vibrational energy is thus included in the ratio between the vibrational partitions functions. R and T have their usual thermodynamic meanings.

If the vibrational partition functions for the conformers are known, then ΔE^m may be estimated from eqn. (1). The *ratio* between the

Table 9. Refined and calculated mean amplitudes (u) of vibration for $(CH_2Br)_4$ at 140 °C.

Type of distance	Dist. (Å)	Calculated[a] u-value (Å)	Refined[b] u-value	σ (Å)
C–H	1.082	0.078	0.098	0.034
C–C	1.552	0.052	0.053	0.010
C–X	1.949	0.057	0.024	0.008
C···C	2.53	0.076	0.065	0.029
$X···X_2$	2.94	0.080	0.068	0.007
$X_1···H_1$	2.47	0.113	0.102	0.036
X···C(g); **D**	3.29	0.164	0.144	0.048
X···C(g); **S**	3.29–3.31	0.145	0.125	(–)[c]
X···C(a)	4.31	0.078	0.088	0.014
X···X(AG); **S**	5.10	0.167	0.152	0.006
X···X(GG); **D**	4.13	0.284	0.270	0.017
X···X(GG); **S**	4.14	0.213	0.199	(–)[c]
X···X(AA); **D**	5.86	0.113	0.099	0.005

[a] The u values correspond to the force field in Table 5. [b] Values obtained by the least-squares refinements. [c] Refined together with the previous value as *one* parameter.

Table 10. Calculations of ΔE^m according to eqn. (1). See text.

	I	II	III
F_ϕ(D), mdyn Å (rad)$^{-2}$	0.33	0.45	0.55
F_ϕ(S), mdyn Å (rad)$^{-2}$	0.86	0.65	0.55
$q=(Q_D/Q_S)^{vib}$	58.8	5.20	1.05
ΔE^m, kcal/mol	+2.51	+0.51	−0.79

partition functions depends on the *difference* in torsional force constants as demonstrated in Table 7. Calculations of ΔE^m using three different sets of torsional force constants are summarized in Table 10. The combination I (0,33, 0.86) corresponds to the torsional force constants determined from the electron diffraction data. The combination II (0.45, 0.65) leads to the value of ΔE^m (0.51 kcal/mol) predicted by the semiempirical energy model. Both experiment and semi-empirical calculations thus indicate that conformer **D** is *less* stable than conformer **S**, but the ΔE^m values do not agree. The possibility III [$F_\phi(D)=F_\phi(S)$] seems less likely, however, a negative value of ΔE^m is not ruled out. The partition-function ratio also depends on conformational differences between non-torsional force constants. Assuming equal values of the vibrational partition functions of the conformers in this molecule could be very wrong.

The difference (**D**−**S**) in zero-point vibrational energy (ΔE_0^{vib}) is −2.1 kcal/mol, while the difference in vibrational energy at 413 K is −1.6 kcal/mol, as calculated from the expression $\Delta E_T^{vib}=RT^2\mathrm{d}(\ln q)/\mathrm{d}T$, with $q=(Q_D/Q_S)^{vib}$ corresponding to the force field in Table 4. The difference (**D**−**S**) in vibrational entropy is +4.3 cal(deg. mol)$^{-1}$ at 413 K, as calculated according to the expression $\Delta S_T^{vib}=R\ln q+RT\mathrm{d}(\ln q)/\mathrm{d}T$. If *equal* values of the conformational force constants are assumed, then ΔE_T^{vib} and ΔS_T^{vib} are temperature *independent* quantities with values close to zero ($q\simeq 1$). The corresponding quantities (ΔE_0^{vib}, ΔE_T^{vib}, and ΔS_T^{vib}) for TMCl [2] have approximately equal values to those reported here for TMBr.

According to the experimental findings the molecules TMCl [2] and TMBr have very nearly a tetrahedral arrangement of C atoms and approximately all-staggered (1:2) low-energy conformations. Conformers possessing parallel (1:3) X···X interactions have significantly higher energies and may deviate considerably from the all-staggered (1:2) form.

The molecular-mechanics calculations reasonably predict the structural parameters for TMBr and TMCl,[2] while the large value of the torsional force constant of the conformer **S** is not predicted by these calculations.

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