Acta Chemica Scandinavica A 28 (1974) 871—884

# Conformational Analysis. VI. The Molecular Structure, Torsional Oscillations, and Conformational Equilibria of Gaseous 1,2,3-Trichloropropane as Determined by Electron Diffraction and Compared with Semi-empirical (Molecular Mechanics) Calculations

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Gaseous 1,2,3-trichloropropane has been studied by electron diffraction at a (nozzle) temperature of 63 °C. Three spectroscopically distinguishable conformers were detected. Results are presented with error limits ($2\sigma$). The following values for bond lengths ($r_g$) and bond angles ($\angle_\alpha$) are average parameters for the conformers: $r$(C—H) = 1.137(22) Å, $r$(C—C) = 1.526(8) Å, $r$(C—Cl) = 1.792(4) Å, $\angle C_1C_2C_3 = 115.2°(2.6)$, $\angle C_2CCl = 110.7°(2.4)$, $\angle CC_2Cl = 110.4°(2.2)$. The torsion angles of the most abundant conformers have been determined.

The composition parameter ($\alpha$) are: $\alpha_4$[GG(ag) + GG(ga)] = 69 % (6), $\alpha_3$[AG(gg) + GA(gg)] = 5 % (8), $\alpha_2$[GA(ag) + AG(ga)] = 26 % (4). The numbering and names of the conformers are shown in Fig. 1. The conformers AA(gg), GG(aa), and GG(gg) are not present in detectable amounts.

It has been demonstrated that torsional force constants can be estimated from the electron diffraction data, if the remainder of the force field is approximately known. The low frequencies ($< 150$ cm$^{-1}$), derived from the electron diffraction data, are in agreement with those spectroscopically observed.

Although the conformational energies predicted by the semi-empirical model seem unlikely, the structure parameters and torsional force constants derived, generally agree with the experimental results.

## I. INTRODUCTION

The present work is one of several in a series of electron diffraction studies 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.

General [1] information [2] relevant to this investigation and to the electron diffraction method [3] is found in Refs. 1, 2, and 3.

The numbering and system of naming for conformers of 1,2,3-trihalopropanes (Fig. 1) was introduced in a previous paper concerned with 1,2,3-tribromopropane (TBP).[4] The numbering of atoms in the conformer GG(ag) is shown in Fig. 2. Unfortunately there is no general agreement about the nomenclature in this type of compounds.

Various authors have reported vibrational spectra of TCP. From Raman spectra [5] it was concluded that only one conformer of TCP was present in the liquid. From infrared spectra [6,7] the presence of at least two conformers in TCP was established. An extended spectroscopic study [8] of 1,2,3-trihalopropanes verified the existence of three or possibly four conformers in the liquids at room temperature. Combined with information from electron diffraction (this work and Ref. 4) of the vapours, the spectra [8] demonstrated the conformer *4* to be present in the low temperature and high pressure crystals of both compounds. This conformer was not the one suggested by earlier authors.[6]

In conclusion, the abundant conformers of TCP and TBP could not be identified by vibrational spectroscopy alone, however, it can be concluded [8] with certainty that the most abundant conformers of the vapours also dominate in the liquids and remain in the crystals.

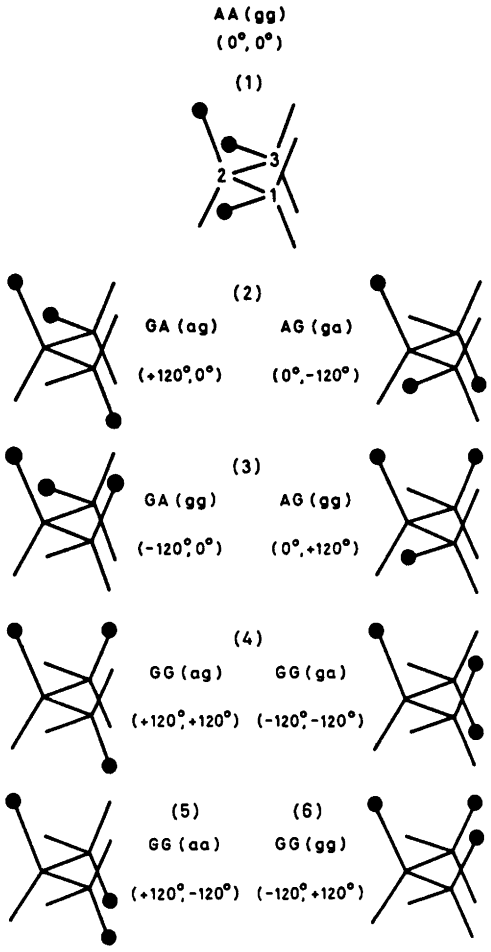


*Fig. 1.* The numbering and names of staggered conformers in 1,2,3-trichloropropane.

## II. MOLECULAR MECHANICS CALCULATIONS OF CONFORMATIONAL ENERGIES, GEOMETRIES, BARRIERS, AND TORSIONAL FORCE CONSTANTS

The method of calculation (the semi-empirical energy model) is described in Ref. 4. Energy parameters ($a$,$b$,$c$,$d$, and $V_0$) were taken from the paper [9] by Abraham and Parry, and the force constants of Table 5 were used. In minimizing the energy, the geometry was constrained in the same way as described in Sect. V-A.

The conformational geometries derived from the semi-empirical model are presented in Table 1.

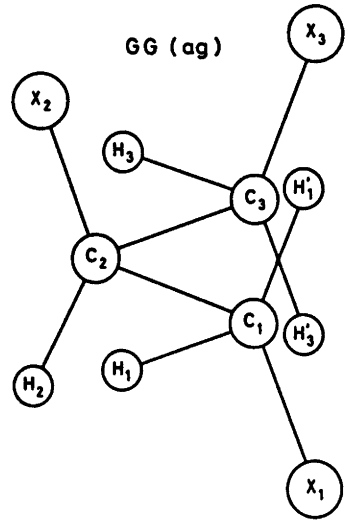


*Fig. 2.* Numbering of atoms in the conformer GG(ag).

Conformational energies of the six spectroscopically distinguishable conformers of TCP are found in Table 2. According to the present energy model *2* is the conformer of lowest minimum energy.

The destabilizing effect of parallel (1:3) Cl···Cl interactions [1] in conformers like GG(aa) and GG(gg) is reproduced by the calculations. The minima of these conformers are considerably displaced from exact staggered torsion angles (Fig. 1).

Torsional barriers may be estimated from the energy values of Table 3. Each energy value of Table 3 corresponds to a conformer having all structure parameters adjusted, except for one or two torsion angles ($\phi$) being kept at constant values. Eclipsed conformers correspond to values of $\phi$ being $\pm 60°$ or $\pm 180°$. The actual values of the geometry variables are not shown in Table 3; however, the values of $\phi_{1-2}$ and $\phi_{2-3}$ are approximately those given in parenthesis. Details about the staggered conformers are found in Tables 1 and 2. The staggered conformers correspond to well defined minima of the potential energy surface.

Valence torsional force constants were computed according to their definitions:

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

*Table 1.* Calculated conformational geometries for 1,2,3-trichloropropane. In minimizing the energy the geometry was constrained as described in Sect. V-A.

| Parameter (normal value) | *4* GG(ag) | *3* AG(gg) | *2* GA(ag) | *1* AA(gg) | *5* GG(aa) | *6* GG(gg) |
|---|---|---|---|---|---|---|
| $r$(C−H), (1.094 Å) | 1.095 | 1.095 | 1.095 | 1.095 | 1.095 | 1.094 |
| $r$(C−C), (1.513 Å) | 1.534 | 1.532 | 1.532 | 1.530 | 1.535 | 1.536 |
| $r$(C−X), (1.780 Å) | 1.792 | 1.793 | 1.792 | 1.794 | 1.789 | 1.793 |
| ∠CCC (110.0°) | 114.1 | 111.8 | 111.2 | 109.0 | 113.8 | 115.2 |
| ∠$C_2$CX (109.47°) | 112.1 | 112.1 | 111.7 | 111.7 | 112.9 | 114.4 |
| ∠$CC_2$X (109.47°) | 110.5 | 111.1 | 109.6 | 110.3 | 108.9 | 112.3 |
| ∠$C_2$CH (109.47°) | 110.0 | 109.8 | 110.0 | 109.8 | 109.8 | 109.0 |
| ∠$CC_2$H (109.47°) | 107.2 | 107.6 | 109.1 | 109.2 | 109.0 | 105.2 |
| $\phi_{1-2}$[a] | +119.0 | +14.4 | +110.9 | +9.3 | +103.4 | −107.7 |
| $\phi_{2-3}$[a] | +122.3 | +122.3 | −8.5 | −9.3 | −103.4 | +107.7 |

[a] $\phi_0 = 60°$ in eqn. (1) in Ref. 4.

*Table 2.* Conformational energies (kcal/mol) for 1,2,3-trichloropropane. Details about the energy expression are found in Ref. 4. The zero-point vibrational energies of the conformers are not included.

| Type of energy | Type of conformer *4* | *3* | *2* | *1* | *5* | *6* |
|---|---|---|---|---|---|---|
| $E$ (bonded) | 1.68 | 1.64 | 1.11 | 1.10 | 2.62 | 4.38 |
| $E$ (van der Waals) | 2.58 | 2.60 | 2.88 | 2.69 | 3.02 | 2.45 |
| $E$ (polar, X···H) | −8.09 | −7.68 | −7.97 | −7.43 | −8.03 | −7.14 |
| $E$ (polar, X···X) | 6.07 | 6.19 | 5.77 | 6.06 | 5.98 | 7.03 |
| $E$ (total) | 2.24 | 2.75 | 1.80 | 2.43 | 3.59 | 6.71 |
| $E$ (tot.) − $E(2) = \Delta E^m$ | 0.44 | 0.96 | 0.00 | 0.63 | 1.79 | 4.91 |

*Table 3.* Calculated conformational energies and torsional barriers in 1,2,3-trichloropropane. Details about the conformational minima corresponding to stable conformers are given in Tables 1 and 2.

| $\phi_{2-3}$(°) | $\phi_{1-2}$(°) −180 | −120 | −60 | 0 | 60 | 120 | 180 |
|---|---|---|---|---|---|---|---|
| 180 | ∞ | 8.9 GG(gg) | 18.6 | 6.7 AG(gg) | 13.7 | 7.6 GG(ag) | ∞ |
| 120 | 8.9 | 4.9 | 10.1 | 1.0 | 4.3 | 0.4 | 8.9 |
| 60 | 18.6 | 10.1 GA(gg) | 17.0 | 10.0 AA(gg) | 13.8 | 9.2 GA(ag) | 18.6 |
| 0 | 6.7 | 1.0 | 10.0 | 0.6 | 3.9 | 0.0 | 6.7 |
| −60 | 13.7 | 4.3 GG(ga) | 13.8 | 3.9 AG(ga) | 7.9 | 3.2 GG(aa) | 13.7 |
| −120 | 7.6 | 0.4 | 9.2 | 0.0 | 3.2 | 1.8 | 7.6 |
| −180 | ∞ | 8.9 | 18.6 | 6.7 | 13.7 | 7.6 | ∞ |

*Table 4.* Calculated torsional force constants ($F_\phi$) for 1,2,3-trichloropropane. The $F_\phi$ values have been numerically computed according to the semi-empirical energy expression.

| Force constant [mdyn Å (rad)$^{-2}$] | (4) GG(ag) | (3) AG(gg) | (2) GA(ag) | (1) AA(gg) |
|---|---|---|---|---|
| $F_\phi(1-2)$ | 0.189 | 0.196 | 0.188 | 0.193 |
| $F_\phi(2-3)$ | 0.270 | 0.220 | 0.188 | 0.193 |
| $F_\phi(1-2;\ 2-3)$ | −0.069 | −0.032 | −0.039 | −0.012 |

*Table 5.* Valence force constants for 1,2,3-trichloropropane.

| | | | |
|---|---|---|---|
| Stretch (mdyn Å$^{-1}$) | | Bend [mdyn Å (rad)$^{-2}$] | |
| C−C | 4.43[a] | CCC | 0.90 |
| $C_1$−H | 4.85 | CCH | 0.67 |
| $C_2$−H | 4.55 | HCH | 0.53 |
| C−X | 3.18 | CCX | 1.17 |
| | | HCX | 0.79 |
| Stretch/stretch (mdyn Å$^{-1}$) (C−C common) | | Stretch/bend [mdyn (rad)$^{-1}$] (C−X common) | |
| C−X/C−C | 0.35 | C−X/CCX | 0.55 |
| C−C/C−C | 0.064 | C−X/HCX (C−C common) | 0.33 |
| Bend/bend [(mdyn Å rad)$^{-2}$] (C−C common) | | C−C/CCX | 0.29 |
| HCC/CCC | −0.12 | C−C/CCC | 0.35 |
| | | C−C/CCH | 0.26 |

Torsion [(mdyn Å rad)$^{-2}$] [b]

| | *4* | *3* | *2* | *1* |
|---|---|---|---|---|
| Conformer | GG(ag) | AG(gg) | GA(ag) | AA(gg) |
| $F_\phi(1-2)$[c] | 0.212 | 0.219 | 0.211 | 0.216 |
| $F_\phi(2-3)$[c] | 0.293 | 0.243 | 0.211 | 0.216 |

[a] Probably, 4.73 would have been a slightly better value for $F$(C−C). [b] 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′−$C_2$−$C_3$−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 $\phi_{1-3}$ (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. [c] These values were estimated from the electron diffraction data as described in Sect. V-B.

The derivatives were calculated numerically at the minimum of potential energy. The values of the force constants are given in Table 4. The interaction force constant $F_\phi(1-2,\ 2-3)$ is always negative and much smaller in absolute value than any of the diagonal ones.

## III. CALCULATION OF VIBRATIONAL QUANTITIES

Valence force constants, except for the torsional part of the force field, were taken from the work [10] of Schachtschneider and Snyder. Certain compromises between force constant values had to be made. The final values selected for TCP are given in Table 5.

The normal-coordinate program described by Gwinn [11] was used in computing vibrational frequencies. Results for some staggered conformers are presented in Table 6 together with the observed spectroscopic frequencies.[8] The torsional part of the force field has been adjusted as described in Sect. V-B.

Keeping in mind the fact that only torsional force constants have been adjusted, the fit between observed and calculated frequencies is very satisfactory. Adjustments of the remainder of the force field were not undertaken. Such

*Table 6.* Fundamental vibrational frequencies ($cm^{-1}$) in conformers (*4,3,2,1*) of 1,2,3-trichloropropane. The force constants of Table 5 were used in calculating frequencies. Structure parameters slightly different from the final ones were used.

| Approximate mode | Observed value [8] | Calculated values *4* | *3* | *2* | *1* |
|---|---|---|---|---|---|
| Torsion | 75 | 68 | 84 | 78 | 76 |
| Torsion | 154 | 131 | 103 | 114 | 121 |
| CCX bend | 206 | 190 | 144 | 182 | 131 |
| CCX bend | 224 | 223 | 246 | 234 | 240 |
| CCX bend | 288 | 298 | 335 | 308 | 284 |
| CCX bend | 356 | 386 | 388 | 406 | 415 |
| CCC bend | 522 | 534 | 541 | 426 | 498 |
| C–X stretch | 622 | 674 | 629 | 679 | 619 |
| C–X stretch | 720 | 725 | 706 | 732 | 704 |
| C–X stretch | 753 | 755 | 758 | 749 | 778 |
| $CH_2$ rock | 872 | 827 | 878 | 851 | 864 |
| $CH_2$ rock | 909 | 925 | 925 | 947 | 953 |
| C–C stretch | 990 | 979 | 975 | 991 | 974 |
| C–C stretch | 1092 | 1125 | 1116 | 1115 | 1092 |
| $CH_2$ twist | 1145 | 1241 | 1241 | 1244 | 1230 |
| $CH_2$ twist | 1200 | 1264 | 1261 | 1248 | 1240 |
| CH def. | 1219 | 1303 | 1296 | 1312 | 1286 |
| $CH_2$ wag | 1282 | 1321 | 1323 | 1322 | 1305 |
| CH def. | 1340 | 1344 | 1340 | 1331 | 1328 |
| $CH_2$ wag | 1292 | 1369 | 1381 | 1369 | 1386 |
| $CH_2$ scissor | 1427 | 1467 | 1466 | 1464 | 1435 |
| $CH_2$ scissor | 1440 | 1483 | 1473 | 1467 | 1438 |
| C–H stretch | 2925 | 2891 | 2891 | 2891 | 2890 |
| C–H stretch | 2960 | 2945 | 2944 | 2945 | 2947 |
| C–H stretch | 2973 | 2945 | 2945 | 2945 | 2947 |
| C–H stretch | 3010 | 3020 | 3020 | 3020 | 3018 |
| C–H stretch | 3020 | 3021 | 3021 | 3020 | 3018 |

adjustments could not lead to any significant changes in mean amplitudes for TCP. Contrary to the situation for TBP,[4,8] the observed spectroscopic torsional frequencies (liquid phase) of TCP agree with the results from electron diffraction. The liquid-phase frequencies are expected to be lower than the gas phase values for torsional modes.

Mean amplitudes of vibration ($u$) and perpendicular amplitude corrections ($K$) were calculated as explained in Ref. 12. The $u$- and $K$ values in conformer GG(ag) are found in Table 7.

Several vibrational quantities in a molecule like TCP varies with the values of the torsional force constants. To illustrate this point, some of these 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. The results are found in Table 8.

## IV. EXPERIMENTAL AND DATA REDUCTION

TCP 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 63 °C in the Balzer [13] apparatus,[14] under conditions summarized below.

*Table 7.* Mean amplitudes ($u$) and $K$ values for the conformer GG(ag) of 1,2,3-trichloropropane at 63 °C. $K$- and $u$ values in Å (See also the text of Table 6). The symbols (a) and (g) means *anti* (a) and *gauche* (g). The numbering of atoms is shown in Fig. 2.

| Distance | $u$ Value (Å) | $K$ Value (Å) | Distance | $u$ Value (Å) | $K$ Value (Å) |
|---|---|---|---|---|---|
| $C_2-H_2$ | 0.0792 | 0.0141 | $X_1\cdots X_3$(a) | 0.0743 | 0.0034 |
| $C_1-H_1'$ | 0.0780 | 0.0230 | $X_2\cdots X_3$(g) | 0.1524 | 0.0051 |
| $C_1-H_1$ | 0.0780 | 0.0226 | $X_1\cdots H_3$(g) | 0.1603 | 0.0107 |
| $C_3-H_3'$ | 0.0780 | 0.0206 | $X_3\cdots H_1'$(g) | 0.1575 | 0.0119 |
| $C_1-C_2$ | 0.0528 | 0.0045 | $X_2\cdots H_1$(g) | 0.1575 | 0.0140 |
| $C_2-C_3$ | 0.0528 | 0.0043 | $X_2\cdots H_3$(g) | 0.1564 | 0.0098 |
| $C_2-X_2$ | 0.0551 | 0.0054 | $X_3\cdots H_3$(a) | 0.1036 | 0.0095 |
| $C_1-X_1$ | 0.0533 | 0.0143 | $X_3\cdots H_3'$(a) | 0.1030 | 0.0103 |
| $C_3-X_3$ | 0.0534 | 0.0131 | $C_3\cdots X_1$(g) | 0.1480 | 0.0049 |
| $C_2\cdots X_1$ | 0.0709 | 0.0081 | $C_1\cdots X_3$(g) | 0.1401 | 0.0060 |
| $C_1\cdots X_3$ | 0.0707 | 0.0047 | $X_1\cdots X_3$ | 0.2516 | 0.0012 |
| $C_3\cdots H_1$ | 0.1079 | 0.0145 | $H_3'\cdots X_1$ | 0.2387 | 0.0138 |
| $C_1\cdots H_3$ | 0.1081 | 0.0092 | $H_3\cdots X_1$ | 0.1625 | 0.0072 |
| $C_1\cdots C_3$ | 0.0723 | 0.0039 | $H_1'\cdots X_3$ | 0.2290 | 0.0177 |
| $H_1\cdots X_1$ | 0.1071 | 0.0239 | $H_1\cdots X_3$ | 0.1686 | 0.0086 |
| $H_2\cdots X_2$ | 0.1079 | 0.0098 | $H_1\cdots H_1'$ | 0.1265 | 0.0301 |

*Table 8.* Vibrational quantities in 1,2,3-trichloropropane at 63 °C.

| | | | |
|---|---|---|---|
| Torsional force constants [a] | | | |
| $F_\phi(1-2)=F_\phi(2-3)=\overline{F}_\phi$, [mdyn Å (rad)$^{-2}$] | 0.12 | 0.25 | 0.48 |
| Torsional frequencies [b] for conformer (*4*), [cm$^{-1}$] | 49<br>100 | 67<br>132 | 85<br>154 |
| Ratios ($q$) between vibrational partitions functions [c] ($Q$) of conformers *1,2,3,4* | | | |
| $Q_4(0.25)/Q_3(\overline{F}_\phi)$ | 0.31 | 0.97 | 3.82 |
| $Q_4(0.25)/Q_2(\overline{F}_\phi)$ | 0.36 | 1.14 | 4.51 |
| $Q_4(0.25)/Q_1(\overline{F}_\phi)$ | 0.36 | 1.00 | 3.92 |
| $u$ Values [d] for the distance $X_1\cdots X_3$, (Å) | | | |
| In conformer *4* | 0.346 | 0.259 | 0.207 |
| In conformer *3* | 0.262 | 0.173 | 0.146 |
| In conformer *2* | 0.261 | 0.171 | 0.144 |
| In conformer *1* | 0.105 | 0.105 | 0.104 |
| $u$ Value for the distance $X_2\cdots X_3$(gauche) in conformer *4* | 0.194 | 0.159 | 0.140 |

[a] See also Table 5. [b] See also Table 6. [c] The $Q$ value of a conformer is referred to the potential-energy minimum of that conformer. [d] See Table 7.

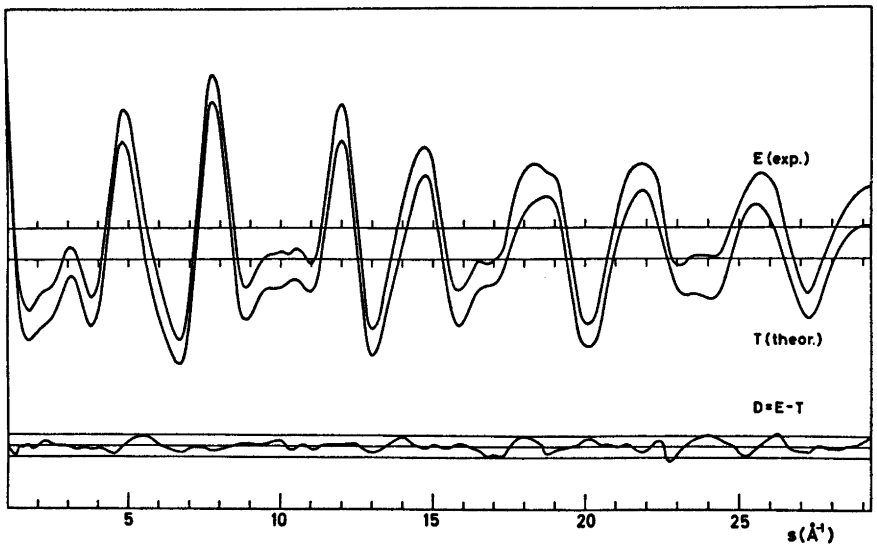


*Fig. 3.* Intensity curves for 1,2,3-trichloropropane at 63 °C. Curve E shows the experimental intensity, and curve T the theoretical intensity corresponding to the final least-squares parameters. Curve D is the experimental minus the theoretical. The straight lines give the experimental uncertainty (±3 × experimental standard deviation).

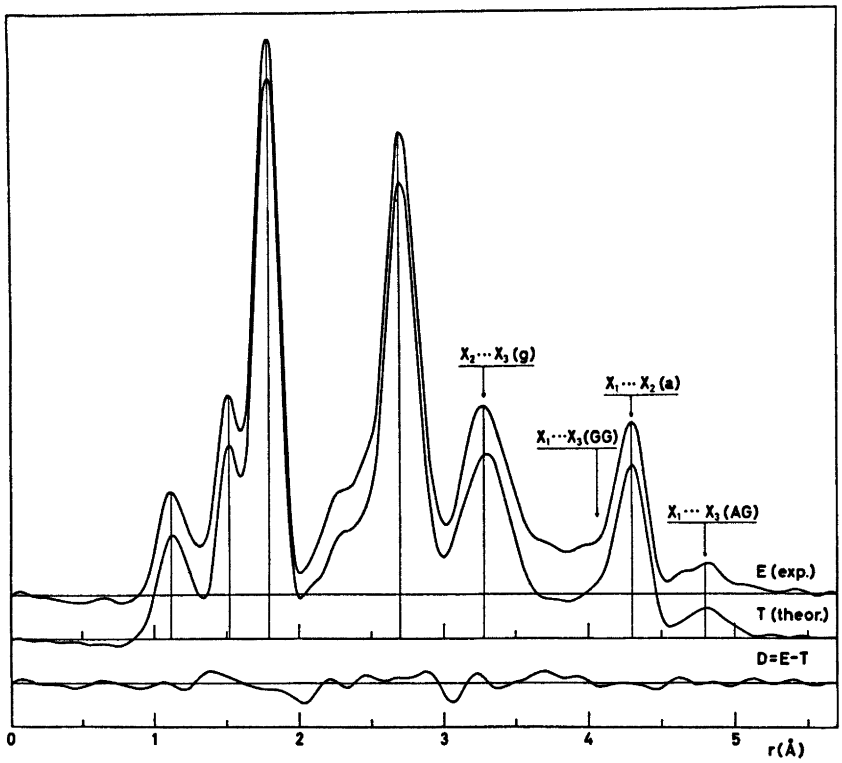


*Fig. 4.* Radial distribution curves for 1,2,3-trichloropropane at 63° C. Experimental (E) and theoretical (T) radial distribution curves and difference curve (D). The RD curves were calculated from the intensity curves of Fig. 3 with and artificial damping constant 0.0020 Å².

| | | |
|---|---|---|
| Nozzle-to-plate distance (mm) | 500.0 | 250.0 |
| Electron wavelength (Å) | 0.05850 | 0.05850 |
| Number of plates | 6 | 6 |
| Range of data, in $s$(Å$^{-1}$) | 1.00 – 15.50 | 2.25 – 29.25 |
| Data interval, $\Delta s$(Å$^{-1}$) | 0.125 | 0.250 |
| Uncertainty in $s$-scale (%) | 0.14 | 0.14 |

The electron wavelength was determined by calibration against ZnO.

The data were reduced in the usual way [15] 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 [15] by $s/|f_C'|\cdot|f_{Cl}'|$. Scattering amplitudes were calculated by the partial wave method [16] using Hartree-Fock atomic potentials.[17]

Radial distribution curves [15] corresponding to Fourier transformation of the final intensity curves are shown in Fig. 4.

## V. STRUCTURE ANALYSIS

The conformational energies computed from the semi-empirical energy model (Sect. II) suggest that the relative amount of conformer *6* is negligible at 63 °C. Conformers *2* and *4* must be expected to be present in detectable amounts. The fact that *4* is the most abundant conformer, and not *2* as suggested by the calculated energies, is obvious from the radial distribution (RD) curves in Fig. 5. From the RD curves it also follows that conformer *1* can hardly be present in detectable amounts. Conformer *3* might be present but in small amounts. The energy calculations suggest that conformer *5* is not present in detectable amounts. In conclusion, it was decided to include the conformers *4*, *3*, and *2* in calculating the theoretical intensities. By trial and error, approximate values for the percentages ($\alpha$) of the conformers were estimated from the experimental RD curve. ($\alpha_4 = 60-70$ %, $\alpha_3 = 0-10$ %, $\alpha_2 = 20-30$ %).

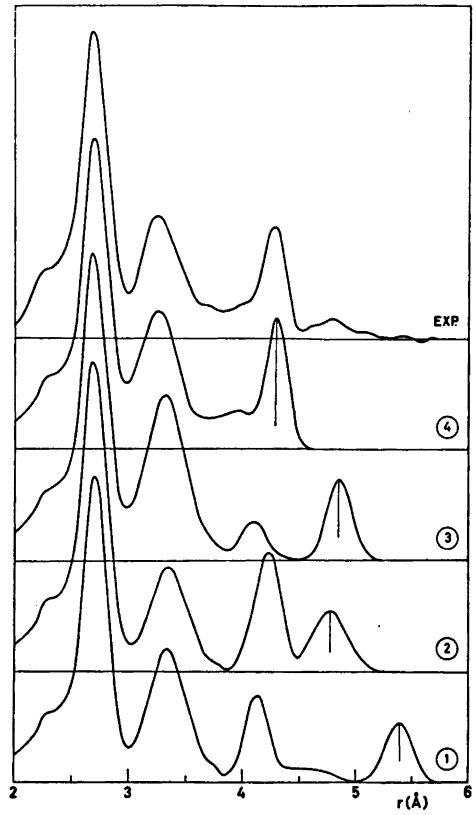


*Fig. 5.* Radial distribution curves for conformers of 1,2,3-trichloropropane at 63 °C. Theoretical RD curves of four conformers and the final experimental one are shown. The theoretical curves have been labelled in the same way as the conformers in Fig. 1. The artificial damping constant was equal to 0.0020 Å$^2$.

*A. Least-squares refinements.* The least-squares program, which is a modified version of the one explained in Ref. 15, was written by H. M. Seip. Several conformers can 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 plane of the $H_2C_2X_2$ group is perpendicular to the plane of the C atoms and bisect the CCC angle; (2) the two $C-CH_2X$ groups are equal; (3) the $C-CH_2X$ groups possess $C_s$ symmetry and, the projection of $\angle H_1C_1H_1$ on the plane perpendicular to the $C_1-C_2$ axis is 120°; (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 ($\phi$); see Fig. 1.

The last assumption is 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 parameters: $r$(C−H), $r$(C−C), $r$(C−X), ∠CCC, ∠$C_2$CX, ∠$CC_2$X, ∠$C_2$CH, ∠$CC_2$H, and the two torsion angles $\phi_{1-2}$ and $\phi_{2-3}$. The torsion angles of the conformers were refined, but not all of them independently. Also adjusted were the composition parameters ($\alpha_4$, $\alpha_3$, and $\alpha_2$), the percentages of the conformers *4*, *3*, and *2*. It was assumed that $\alpha_1=\alpha_5=\alpha_6=0$ %.

Corrections for the "Bastiansen-Morino" shrinkage [18] 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.[19,20]

*B. Determination of torsional force constants.* Torsional force constants were not known for TCP, however, some of the mean amplitudes of vibration ($u$) get considerable contribution from the torsional modes. (Torsional modes also contribute substantially to some of the $K$ values.) Therefore, since a reasonable force field is known, except for the torsional force constants, the latter can be adjusted to fit the experimental intensities. This procedure worked out well in the case of TBP.[4]

Determination of all torsional force constants from the electron diffraction data alone, is not possible. Therefore, the theoretical values of Table 4 were used as a guide, and the following assumptions were introduced:

(1) all interaction constants $F_\phi(1-2, 2-3)=0$;
(2) $F_\phi=F_\phi$(calc.)$+\Delta F_\phi$ for all conformers.

Thus, the differences between the diagonal force constants are those of Table 4. $\Delta F_\phi$ was adjusted, as follows. Parallel and perpendicular amplitudes corresponding to several values of $\Delta F_\phi$ were computed and included in the least-squares refinements. The structures and composition parameters were refined simultaneously for each new value of $\Delta F_\phi$. The best fit between theoretical and experimental intensities was obtained for $\Delta F_\phi$ equal to $+0.023$ mdyn Å (rad)$^{-2}$. The final values of the torsional force constants are shown in Table 5.

It is difficult to estimate realistic uncertainties in the $F_\phi$ values.[4] The differences between the force constants have not been varied, only the parameter $\Delta F_\phi$ was adjusted. Moreover, systematic errors in the remainder of the force field will certainly lead to systematic errors in the $F_\phi$ values as determined here. The values of the force constants F(CCC) and F(CCX) seem to be the critical ones in this respect, but their values are probably close to the correct values for TCP (see Table 6).

In conclusion, the most probable range for the torsional force constants is: 0.2 − 0.3 mdyn Å (rad)$^{-2}$. The values of $F_\phi$ (0.19 − 0.27) predicted by the semi-empirical model (Table 4) are therefore not unlikely.

## VI. FINAL RESULTS

Parameters from the least-squares refinements and standard deviations ($\sigma$) corrected for correlation [21] in the experimental data are given. In the final refinements 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 internuclear distances.

*Table 9.* Bond lengths ($r_a$) and bond angles (∠$_\alpha$) *in 1,2,3-trichloropropane (X=Cl).* Standard deviations are given in parentheses.

| Bond lengths (Å) | Bond angles (°) |
|---|---|
| $r$(C−H) = 1.131(11) [a] | ∠CCC = 115.2(1.3) [b] |
| | ∠$C_2$CX = 110.7(1.2) |
| $r$(C−C) = 1.524(4) | ∠$CC_2$X = 110.4(1.1) |
| | ∠$C_2$CH = 110.8(3.5) [c] |
| $r$(C−X) = 1.790(2) | ∠$CC_2$H = 107.0(4.4) [c] |

[a] An experiment with $CO_2$ gave a correction of 0.1 % in the $s$-scale. The bond lengths are therefore 0.1 % longer than those directly determined by the refinements. The uncertainty (0.14 %) in the $s$-scale has been included in the standard deviations of bond lengths. [b] The bond angles are those of the selfconsistent $r_\alpha$ structure. The *dependent* bond angles are ∠$XC_1H$ = 108.2°(2), ∠$HC_1H$ = 108.1°(5), and ∠$XC_2H$ = 106.4°(2). [c] These values are the results of a refinement with $\phi$ angles, ∠CCC, ∠$C_2$CX, ∠$CC_2$X, and $u$ values of nonbonded distances not refined.
Parameter correlation ($\varrho$), with $|\varrho|>0.49$:
$\varrho(CC_2X/C_2CX) = -0.99$; $\varrho(CC_2H/C_2CH) = -0.84$

*Table 10.* Torsion angles ($\phi$) and composition (63 °C) parameters ($\alpha$) of 1,2,3-trichloropropane. Standard deviations are given in parentheses.

| Conformer | *2* | *3* | *4* |
|---|---|---|---|
| $\alpha$ | 26 % (2)[a] | 5 %(4) | 69 %(3)[a] |
| | GA(ag) | AG(gg) | GG(ag) |
| $\phi_{1-2}$ | $102.2° = (110.9° - \phi_2)$ | $(+14.4°)$ | $116.8° = (119.0° - \phi_4)$ |
| $\phi_{2-3}$ | $-17.2° = (-8.5° - \phi_2)$ | $(+122.3°)$ | $124.5° = (122.3° + \phi_4)$ |
| | $\phi_2 = 8.7°(3)$[b] | – | $\phi_4 = 2.2°(2)$[b] |

[a] The parameters $\alpha_2$ and $\alpha_4$ were refined with $\alpha_3 = 100\ \% - \alpha_2 - \alpha_4$. [b] The parameters $\phi_2$ and $\phi_4$ were refined but not simultaneously. The torsion angles of conformer (*3*) were taken from Table 1.
Parameter correlation ($\varrho$), with $|\varrho| > 0.49$:

$\varrho(\alpha_2/C_3CX) = -0.74$; $\varrho(\alpha_2/CC_2X) = 0.74$; $\varrho(\alpha_2/u_3) = 0.52$; $\varrho(\alpha_2 u_a) = 0.60$; $\varrho(\alpha_2/u_g) = -0.82$; $\varrho(\alpha_2/u_{13}') = -0.63$; $\varrho(\alpha_2/u_{13}) = 0.77$ $u_3 = u(C_3 \cdots X)$; $u_a = u(X \cdots X$, anti); $u_{13}' = u(X_1 \cdots X_3)$ in conformer *2*; $u_{13} = u(X_1 \cdots X_3)$ in conformer *4*; $u_g = u(X \cdots X$, gauche).

*Table 11.* Mean amplitudes of vibration ($u$) at 63 °C for 1,2,3-trichloropropane.

| Distance type | Approx. dist. (Å) | Refined $u$ value (Å) | Standard[a] deviation | Calculated[b] $u$ value (Å) |
|---|---|---|---|---|
| C–H | (1.13) | 0.070 | 0.011 | 0.078 |
| C–C | (1.52) | 0.049 | 0.006 | 0.053 |
| C–X | (1.79) | 0.044 | 0.003 | 0.054 |
| $C_3 \cdots X_1$ | (2.72) | 0.073 | 0.005 | 0.071 |
| $C_1 \cdots X_3$ | (2.71) | (0.073)[c] | (0.005)[c] | (0.071) |
| $H_1 \cdots X_1$ | (2.38) | 0.103 | 0.018 | 0.107 |
| $H_2 \cdots X_3$ | (2.36) | (0.104)[c] | (0.018)[c] | (0.108) |
| X···X (anti) | | | | |
| in conformer *4* | (4.31) | 0.069 | 0.009 | 0.074 |
| in conformer *2* | (4.28) | (0.076)[c] | (0.009)[c] | 0.081 |
| X···X (gauche) | | | | |
| in conformer *4* | (3.34) | 0.145 | 0.010 | 0.152 |
| in conformer *2* | (3.34) | (0.156)[c] | (0.010)[c] | 0.163 |
| $X_1 \cdots X_3$ | | | | |
| in conformer *4* | (4.06) | 0.264 | 0.024 | 0.252 |
| in conformer *2* | (4.76) | 0.135 | 0.025 | 0.179 |

[a] The standard deviations are those from the least-squares refinements. [b] The valence force constants are given in Table 5. [c] This value was refined together with the previous value as *one* parameter.
Parameter correlations ($\varrho$), with $|\varrho| > 0.8$:

$\varrho(u_g/C_3CX) = 0.88$; $\varrho(u_g/CC_2X) = -0.86$; $u_g = u(X \cdots X$, gauche); $\varrho(u_{13}/C_3CX) = -0.91$; $\varrho(u_{13}/CC_2X) = 0.89$; $u_{13} = u(X_1 \cdots X_3)$ in conformer *4*; $\varrho(u_{13}/u_g) = -0.94$; $\varrho(u_{13}'/u_{13}) = -0.81$; $u_{13}' = u(X_1 \cdots X_3)$ in conformer *2*.

Parameter correlation [15] coefficients ($\varrho$) are included in Tables 9–11. The average bond lengths and bond angles are found in Table 9.

Several refinements were carried out in order to determine the torsion angles ($\phi$), not all of them being successful. Finally, the angles were restricted under constraints which are shown together with the values in Table 10. Two parameters, $\phi_2$ and $\phi_4$ were adjusted, and their meaning is understood when comparing Fig. 1 with the relations in Table 10. The parameters $\phi_2$ and $\phi_4$ measure the deviations from values predicted by the semiempirical model. For conformer *3*, the calculated $\phi$ values were assumed.

The refined $\phi$ values and those calculated for conformer *4* are not significantly different. [$\phi_4 = 2.2°$ and $\sigma(\phi_4) = 2°$]. The value of $\phi_2$ is significantly different from 0°. The torsion angles of both conformers are different from exact staggered values, but the deviations within conformer *4* are quite small.

Composition parameters ($\alpha$) from the least-squares refinements are given in Table 10. The conformers *4* and *2* are clearly present in significant amounts, but the low percentage (5 %) of conformer *3* is not significantly different from zero. [$\sigma(\alpha_3) = 4$ %.] The presence of a small percentage of conformer *1* could not be disproved by including that conformer in the refinements. Contributions ($\alpha_1$) of conformer *1* were included in the least-squares refinements. The parameter $\alpha_1$ was adjusted, with $\alpha_4 = 69\ \% - 0.5\alpha_1$, $\alpha_3 = 5$ %, and $\alpha_2 = 26\ \% - 0.5\alpha_1$. Several values of $\alpha_1$ from 0 % to 10 % was tried. The best fit was obtained with $\alpha_1$ close to 0 %. A small percentage (0–5 %) of confomer *1* is possible; however, a large relative amount of *1* is ruled out.

Mean amplitudes ($u$) from least-squares refinements [15] and those determined by adjusting the torsional force constants (Sect. V-B) are compared in Table 11. The $u$ values which are not found in Table 11 could not be refined as individual parameters, but their values have been adjusted in adjusting the torsional force constants. (Sect. V-B) These $u$ values, and the corresponding $K$ values, are found in Table 7.

The average relative deviation ($\Delta u/u$), between the two sets of $u$ values is *ca.* 10 %, while the average relative uncertainty, ($\sigma/u$), of the refined $u$ values is *ca.* 12 %. The mean amplitudes calculated with the final force constants seem the more reliable set of $u$ values.

Cartesian coordinates for the conformers *4* and *2* together with the principal axes' moments of inertia are given in Table 12.

The intensities and radial distribution curves, corresponding to the final parameters, are found in Figs. 3 and 4, respectively.

## VII. DISCUSSION

The percentages $\alpha^*$ and $\alpha$ of two conformers in equilibrium in the gas phase (C⇌C*) are related to the theoretical [22] expression [23] for the equilibrium constant, as given in eqn. (1):

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

The six *spectroscopically* distinguishable conformers (see Fig. 1) have been assigned a multiplicity M. The value of M is *one* for the conformers *1*, *5*, and *6*, and *two* for the conformers *2*, *3*, and *4*. $Q^{\mathrm{vib}}$ is the vibrational partition function [22,23] of a conformer referred to the potential-energy minimum of that conformer. (The classical [22,23] rotational partition functions of the conformers are approximately equal.) $\Delta E^{\mathrm{m}} = E^* - E$ is the potential-energy difference between conformer C* and C, and the difference is measured between energy minima. The zeo-point vibrational energy is included in the quantity $Q^{\mathrm{vib}}$. $R$ and $T$ have their usual thermodynamic meanings.

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

According to the semi-empirical energy model (Table 2), *2* is the conformer of lowest minimum energy. If the $\Delta E^{\mathrm{m}}$ values of Table 2 are accepted, then the ratios between the vibrational partition functions of the conformers have to be quite different from 1.0, as shown in Table 13 (I). On the other hand, if the conformers have equal vibrational partition functions ($q = 1$), the $\Delta E^{\mathrm{m}}$ values of Table 13 (II) show that *4* is the conformer of lowest minimum energy.

In order to explain the experimental composition (Table 10), two possibilities have to be considered: (I) the conformational energies

*Table 12.* Cartesian coordinates (Å) for the most abundant conformers of 1,2,3-trichloropropane. The coordinates have been calculated using the final $\angle_\alpha$ values for angles and $r_g$ values ($r_g = r_a + u^2/r$) for bond lengths: (C–H: 1.137 Å, C–C: 1.526 Å, C–Cl: 1.792 Å). The numbering of atoms in the conformer GG(ag) is shown in Fig. 2. The principal axes' moments of inertia (amu Å²) are:

$I_A = 255.1$, $I_B = 398.4$, and $I_C = 585.5$ for *4*:GG(ag)
$I_A = 183.0$, $I_B = 501.0$, and $I_C = 610.8$ for *3*: AG(gg)
$I_A = 236.1$, $I_B = 484.0$, and $I_C = 682.9$ for *2*:GA(ag)
$I_A = 139.7$, $I_B = 593.1$, and $I_C = 682.2$ for 1:AA(gg)

| *4*, conformer GG(ag) | | | Atom | *2*, conformer GA(ag) | | |
|---|---|---|---|---|---|---|
| *x* | *y* | *z* | No. | *x* | *y* | *z* |
| 0 | 0 | 0 | $C_3$ | 0 | 0 | 0 |
| 1.2884 | 0.8177 | 0 | $C_1$ | 1.2884 | 0.8177 | 0 |
| 1.4183 | 1.7952 | −1.4963 | $X_1$ | 1.6335 | 1.4562 | −1.6385 |
| 1.3174 | 1.5255 | 0.8894 | $H_1'$ | 1.2074 | 1.6989 | 0.7140 |
| 2.1980 | 0.1380 | 0.0594 | $H_1$ | 2.1716 | 0.1795 | 0.3249 |
| −1.2884 | 0.8177 | 0 | $C_2$ | −1.2884 | 0.8177 | 0 |
| −1.3145 | 1.9587 | 1.3815 | $X_3$ | −2.6813 | −0.1949 | −0.4957 |
| −1.3841 | 1.4204 | −0.9593 | $H_3'$ | −1.5031 | 1.2328 | 1.0365 |
| −2.1971 | 0.1393 | 0.0834 | $H_3$ | −1.2114 | 1.6925 | −0.7222 |
| 0 | −1.1656 | 1.3611 | $X_2$ | 0 | −1.1656 | 1.3611 |
| 0 | −0.6204 | −0.9528 | $H_2$ | 0 | −0.6204 | −0.9528 |

*Table 13.* Energy differences, $\Delta E^m$(kcal/mol), and ratios ($q$) between vibrational partition functions of the conformers *4*, *3*, and *2* of 1,2,3-trichloropropane at 63 °C.

| Difference(−) or ratio(/) | (*4*) (*3*) | (*4*) (*2*) | (*3*) (*2*) |
|---|---|---|---|
| $\Delta E^m$ (calc.)[a]; see Table 2 | −0.52 | +0.44 | +0.96 |
| (I) Ratio ($q$)[b] between vibrational partition functions; if $\Delta E^m$ (calc.) values are used | 6.1 | 5.0 | 0.82 |
| (II) $\Delta E^m$ Values[c]; if $q = 1$ | −1.75 | −0.65 | +1.10 |

[a] $\Delta E^m$ (calc.) is the conformational-energy difference (between energy minima) predicted by the semi-empirical model (Sect. II). [b] $q = (Q^*/Q)^{vib}$, calculated according to eqn. (1). $Q^{vib}$ is the vibrational partition function of a conformer referred to the energy minimum of that conformer. [c] Calculated according to eqn. (1). The nozzle temperature (63 °C) and the composition parameters ($\alpha$) of Table 10 were used.

($\Delta E^m$) predicted by the semi-empirical calculations are approximately correct, but conformer *4* has a much lower zero-point vibrational energy than the conformers *2* and *3*; (II) the conformers have approximately equal zero-point vibrational energies ($q \simeq 1$), but then the $\Delta E^m$ values have to be quite different from those predicted by the semi-empirical model.

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? Vibrational spectroscopy, at present, can not prove or disprove this possibility since a complete set of fundamental experimental frequencies [8] does not exist. From the values of Table 8 it is concluded that large differences in torsional force constants between the conformers may lead to $q$ values as large as 5–6. Although such large differences are possible, it seems not very likely for a molecule like TCP. Large differences within the remainder of the conformational force fields are not ruled out, but that seems even less likely. An indication of conformer *2* having much larger torsional force constants than conformer *4* is found in Table 11. The refined mean amplitude of vibration ($u$) of the distance $X_1 \cdots X_3$ in conformer *2* is much lower

(0.135 Å) than the value (0.179 Å) corresponding to nearly equal torsional force constants. In order to obtain a value as low as 0.135 Å, the torsional force constants of conformer *2* would have to be larger than 0.5 mdyn Å (rad)$^{-2}$, which seems very unlikely. Unfortunately, this $u$ value and the corresponding one for conformer *4* are very uncertain quantities. (The difference between 0.179 Å and 0.135 Å is less than *two* standard deviations.) In conclusion, the first possibility seems unlikely, but the second possibility is not proved thereby. The correct values of $\Delta E^{m}$ are probably a compromise between the two sets I and II.

Although the conformational energies predicted by the semi-empirical model seem unlikely, the structure parameters and torsional force constants generally agree with the experimental results.

It has been demonstrated that torsional force constants of TCP can be estimated from the information of the electron diffraction data, if the remainder of the force field is known. The most probable range for the torsional force constants is: 0.2 – 0.3 mdyn Å (rad)$^{-2}$. Values outside this range are less likely. For conformer *4* the average torsional force constant ($\overline{F}_{\phi}$) and the torsional frequencies ($\omega_1$ and $\omega_2$) are:

$$\overline{F}_{\phi} = 0.25^{+0.20}_{-0.10} \text{ mdyn Å (rad)}^{-2},$$
$$\omega_1 = 67 \pm 15 \text{ cm}^{-1}$$

and $\omega_2 = 132 \pm 20$ cm$^{-1}$ (see also Sect. V-B). It has already been pointed out that the low frequencies of 1,2,3-trihalopropanes derived from the electron diffraction data are in good agreement with the spectroscopically observed values, (Table 6) for TCP, while a new assignment has been proposed for TBP.[4] The values of $F_{\phi}$ predicted by the semi-empirical energy model (Table 4) are not significantly different from those derived from the information of the electron diffraction data.

The electron diffraction studies of 1,2,3-trihalopropanes have lead to several conclusions relevant to the spectroscopic investigations of these and similar compounds: (1) the wrong spectroscopic conclusion,[6] listing conformer *2* as the most abundant one in TCP, has been corrected; (2) the empirical C-halogen group-frequency correlations break down [8] for TCP and TBP; (3) low torsional frequencies (50 – 150 cm$^{-1}$) in the most abundant conformers are available from the electron diffraction data of the gas phase; (4) the final adjustment of force constants ought to take into account the information derived from electron diffraction data.

Clearly, *4* is the most abundant conformer in both TCP and TBP.[4] The conformer *4*, in both compounds, is nearly staggered. The CCC angles (115 – 118°) are significantly larger than that of propane, while the C – C bond lengths (*ca.* 1.53 Å) are not significantly different from the one in propane itself. In conclusion, the large Cl and Br atoms, when substituted in the 1,2,3-positions, lead to a rather large increase of the CCC bond angle, while the terminal groups remain nearly staggered.

*Note added in proof:* A recent analysis [24] of the NMR spectra of $XH_2C-CHX-CH_2X$ (X = Cl, Br) in the liquid phase leads to conformational distributions which agree with the gas-phase distributions.

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

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Received April 1, 1974.