

Determination of the Conformational Composition and Molecular Structure of Gaseous *cis,cis*-1,4-Dichloro-1,3-butadiene by Electron Diffraction

Grete Gundersen,^a Fred Karlsson,^b Zuzana Smith^b and Hanne G. Thomassen^a

^aDepartment of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo 3, Norway and ^bArrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden

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The *anti* conformer ($\varphi_a = 180^\circ$) was, as expected, found to predominate in gaseous *cis,cis*-1,4-dichloro-1,3-butadiene, but a *gauche* form ($\varphi_g \approx 60^\circ$) was also identified in small amounts: 4 (3), 5 (3) and 10 (4) % at 283, 314 and 473 K, respectively. This corresponds to *anti-gauche* energy and entropy differences of $\Delta E^\circ = E_g^\circ - E_a^\circ = 6$ (5) kJ mol⁻¹ and $\Delta S_g^\circ = S_g^\circ - S_a^\circ - R \ln 2 = -10$ (15) J mol⁻¹ K⁻¹.

The *gauche* torsional angle was determined from the high temperature data, $\varphi_g = 59(12)^\circ$. The intermediate temperature data gave the following geometrical parameters (r_a and \angle_a): $r(\text{C-H}) = 110.5$ (7), $r(\text{C=C}) = 134.2$ (2), $r(\text{C-C}) = 145.6$ (4), $r(\text{C-Cl}) = 173.1$ (3) pm; $\angle \text{C=C-C} = 125.1$ (3), $\angle \text{C=C-Cl} = 123.7$ (2), $\angle \text{C=Cl-H} = 124.5$ (13), and $\angle \text{C-C-H} = 116$ (2) $^\circ$. Refinements of a framework structure and the root-mean-square torsional angle amplitude, δ , for the *anti* form gave similar fit to the data, and $\delta = 11.4$ (10) $^\circ$ which corresponds to a torsional force constant of 0.11 aJ rad⁻² as compared to the vibrational spectroscopic value of 0.13 aJ rad⁻². The 283 and 473 K data, which were obtained with a low pressure nozzle and reduced data range yielded torsional force constants of 0.06 and 0.07 aJ rad⁻². The use of low pressure nozzles seems to lead to discrepancies between vibrational parameters determined by electron diffraction and spectroscopy, but the geometrical parameters appeared unaffected in the present study.

It is well established that gaseous 1,3-butadiene exists predominately in a planar *anti* conformation ($\varphi (\text{C=C-C=C}) = 180^\circ$). Its molecular structure has been determined by gas phase electron diffraction (GED).¹⁻³ The conformational behaviour of 1,3-butadiene has, however, been a matter of controversy throughout the last few decades. Both the form of a possible coexisting second conformer in the gas and its relative energy have been debated.⁴⁻⁵ The second conformer could be in a planar *syn* ($\varphi = 0^\circ$) or a nonplanar *syn* form, also referred to as *syn* and *gauche* respectively. As discussed elsewhere,⁴ early GED data appeared to suggest a conformational mixture with a *gauche* form as the less abundant con-

former, but no conclusive new evidence was published. The consensus of recent publications based on spectroscopic and theoretical studies⁵⁻¹³ seems to be that the second energy minimum appears for the *nonplanar syn* form. The reported values for the *gauche* angle are in the range of 20–40 $^\circ$. It has also been suggested that the barrier of rotation to the *syn* form is very low, which, together with its low abundance, make the characterization of the *gauche* form by experimental methods extremely difficult. In fact, recent GED experiments at various temperatures (20–900 $^\circ\text{C}$)¹⁴ failed to identify a second form, but could not rule out the presence of an additional potential minimum at least 15 kJ mol⁻¹ above

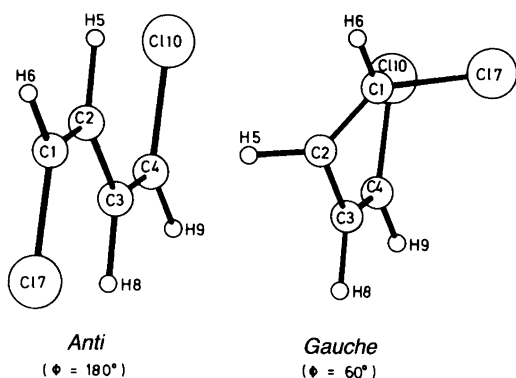


Fig. 1. Views of an *anti* and a *gauche* form of *cis,cis*-1,4-dichloro-1,3-butadiene with numbering of the atoms. The *gauche* form is twisted 60° from the *syn* conformation of $C1=C2-C3=C4$.

anti. By comparison, the energy difference values obtained in recent *ab initio* MO calculations^{6,10} are in the region 11–13 kJ mol⁻¹. GED has, however, identified small amounts of *gauche* forms of two substituted 1,3-butadienes which contain predominately the *anti* conformers: 2-methyl-1,3-butadiene has 4.7% *gauche* ($\varphi = 73.5^\circ$) at room temperature;¹⁵ and 2,3-dichloro-1,3-butadiene is found to have 2.8 (67), 7.3 (63) and 16.1 (58)%

gauche ($\varphi = 52 (10)^\circ$) at 293, 395 and 593 K, respectively, which correspond to an *anti-gauche* energy difference of 9.2 kJ mol⁻¹.¹⁶ In this paper, we report the results of a GED investigation of *cis,cis*-1,4-dichloro-1,3-butadiene (see Fig. 1) for which vibrational spectroscopic data have been interpreted in terms of a prevailing *anti* ($\varphi = 180^\circ$) conformer.^{17,18}

Experimental and data processing

A pure sample of *cis,cis*-1,4-dichloro-1,3-butadiene, hereafter referred to as CC2, was obtained as described elsewhere.¹⁸

Electron diffraction scattering diagrams were recorded on Kodak electron image plates using the Oslo diffraction apparatus¹⁹ and an accelerating voltage of about 35 kV. The electron wavelength (s scale) was calibrated against diffraction patterns of gaseous benzene using $r_s(C=C) = 139.75$ pm as a standard;²⁰ the estimated uncertainty $\approx 0.1\%$. Further experimental details for three data sets each of two nozzle-to-plate distances are given in Table 1. Initially, the experiment was carried out using a conventional nozzle and a nozzle temperature of 314 K (set B). Subsequently, it became clear that high temperature data were needed for further elucidation of the

Table 1. Experimental conditions for *cis,cis*-1,4-dichloro-1,3-butadiene.

Data set:	A: 283 K		B: 314 K		C: 473 K	
Nozzle temperature						
Nozzle-to-plate distance (mm)	484.78	334.78	477.68	197.68	484.78	334.78
Electron wave length (pm)	6.466	6.466	6.470	6.470	6.466	6.466
No. of plates	2	2	5	5	2	2
Data range						
s_{min} (nm ⁻¹)	20.0	40.0	20.0	80.0	20.0	40.0
s_{max} (nm ⁻¹)	180.0	270.0	197.5	390.0	180.0	270.0
Δs (nm ⁻¹)	1.25	2.5	1.25	2.5	1.25	2.5
Data weighting ²⁴						
$s1$ (nm ⁻¹)	50.0	50.0	50.0	80.0	50.0	50.0
$s2$ (nm ⁻¹)	120.0	150.0	197.5	250.0	120.0	150.0
$w1$ (10 ⁻⁴ nm ²)	15	15	15	0	15	15
$w2$ (10 ⁻⁴ nm ²)	23	1	0	1	23	1

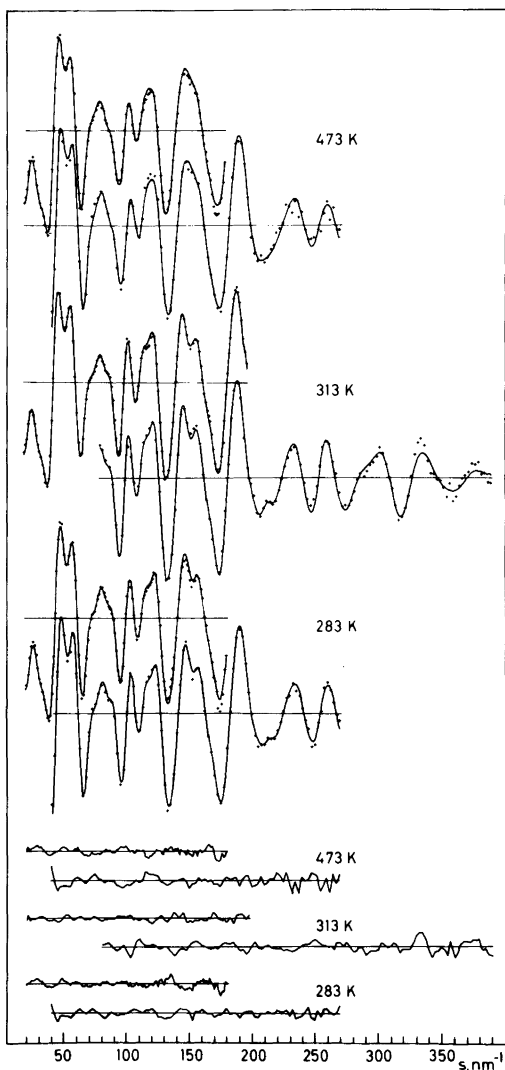


Fig. 2. Observed (·) and final theoretical (—) and difference (below) molecular intensity curves for *cis,cis*-1,4-dichloro-1,3-butadiene at 3 temperatures each at 2 camera distances (Table 1).

conformational properties of CC2. Such data were at the time only obtained by the use of a low pressure (doughnut) nozzle^{21,22} which could be used for temperatures up to 473 K. Two new sets of data were recorded (A, 283 K and C, 473 K) to ensure consistent experimental conditions for two temperatures. The s range was somewhat reduced due to sample limitations (Table 1).

The optical densities of the diagrams for set B were recorded in intervals of 0.25 mm while oscillating the plates on an integrating densitometer constructed by A. Almendingen and P. Molén. For A and C, a modified Joyce-Loebl microdensitometer at the Department of Astrophysics was used to record a raster image of the diagrams, and each of the two plates for each of the four distance/temperature combinations was photometered twice.

The data reduction was carried out using standard computer programs. The blackness corrections were: set A and C, $0.96 - 0.182D + 0.113D^2 - 0.012D^3$; set B, $1.0 - 0.047D + 0.1D^2 - 0.013D^3$. An automatic background subtraction procedure, analogous to that described by L. Hedberg,²³ was used for each individual curve on the $s/|f_c|^2$ modified form.²⁴ The resulting modified molecular intensities were then averaged for each data set giving the six experimental intensity curves shown in Fig. 2. The least-squares structural analyses were based on these data using diagonal weight matrices as defined in Table 1, and giving each of the two curves for each set equal weight. However, the standard deviations thus obtained (σ_{cs}) should be augmented by a factor of 2 to account for correlation in the data, as suggested by comparative least-squares refinements using diagonal weight matrices and nondiagonal ones with standard values for the nondiagonal elements.²⁵

Experimental radial distribution (RD) curves (Fig. 3) were calculated for each of the three data sets by scaling and averaging the intensity values in the overlap region for the two camera distances and using pertinent theoretical intensity values for the unobserved inner region, i.e. for $s < s_{\min}$ of Table 1.

The scattering amplitudes, $|f^r(s)| = \frac{1}{2}a_0s^2|f(s)|$ and phases, $\eta(s)$, were calculated using the partial wave method²⁶ and analytical HF potentials for carbon and chlorine²⁷ and the best electron density for bonded hydrogen.²⁸ The inelastic scattering factors used were those of Tavard *et al.*²⁹

Structure analysis

Geometrical and vibrational models. Views of the molecule showing the atom numbering are presented in Fig. 1. The geometry of one conformer of CC2 is described by nine parameters, assuming the two types of spectroscopically different

C-H bonds (C_1-H and C_2-H) to be of equal length. The parameters are defined in Table 2. To provide possibilities for a two-conformer interpretation of the data, a second torsional angle (φ_2) and a composition parameter α_2 (mole fraction of the second conformer) were included. It was then assumed that any two conformers would differ geometrically only in the torsional angle. The possibility for a dynamic model description for the *anti* form was also implemented by using the rms amplitude of the torsional vibration, δ , as a parameter. When this parameter was used in the specification of the CC2 system, i.e. set different from zero or refined, the *anti* form was treated as a mixture of five pseudoconformers with torsional angles $\varphi_1^i = 180^\circ \pm \Delta\varphi^i$ where $\Delta\varphi^i = 0, \frac{1}{2}\delta,$

$\delta, \frac{3}{2}\delta,$ and 2δ ; each with weights $P(\varphi) = Q^{-1} \exp [-(\Delta\varphi)^2/2\delta^2]$.³⁰

The CC2 system is also described by a large number of vibrational amplitude parameters (rms amplitudes: l values). Some of these were assigned values as calculated from a literature valence force field¹⁸ at the appropriate temperatures, and some were refined in groups in which the *relative* magnitudes of the amplitudes correspond to the calculated values. Since there are no spectroscopic data for a higher energy form, the same force field was used for calculations of vibrational amplitude quantities for the second form using coordinates corresponding to appropriate φ_2 values. Anharmonicity constants, κ , were included²⁴ for the bonds only. The values were estimated from the diatomic approximation³¹ using $\kappa = 1/6a_3 l^3$ where $a_3 = 20 \text{ nm}^{-1}$; the l values are as calculated from the valence force field for CC2.

A r_α model was used to account for shrinkage effects. The geometry is then described by r_α type parameters (Table 2) and the geometrically consistent set of r_α interatomic distances are con-

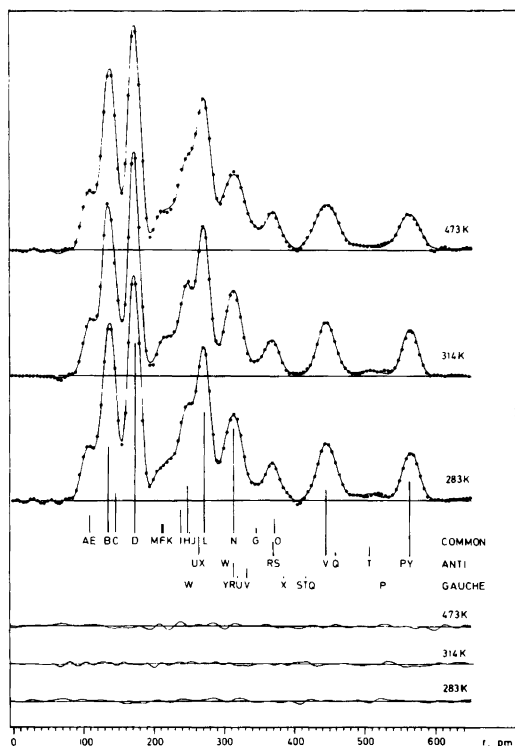


Fig. 3. Experimental (·), final theoretical (—) and difference (---) radial distribution curves of *cis,cis*-1,4-dichloro-1,3-butadiene at three temperatures. The damping coefficient is $1.5 \cdot 10^{-5} \text{ nm}^2$. The distance distribution is indicated by the vertical bars. The capital letters refer to the distances in Table 3, and they are separated in three categories: *a*, common, *b*, *anti*, and *c*, *gauche*.

Table 2. Results for the structural parameters of *cis,cis*-1,4-dichloro-1,3-butadiene. Distances (r_α) in pm and angles (\angle_α and φ_α) in degrees.^a

Parameter	A: 273 K	B: 314 K	C: 473 K
$p1$: C-H	107.3(7)	109.0(7)	107.1(8)
$p2$: C=C	133.9(15)	133.5(3)	133.7(5)
$p3$: C-C	145.9(3)	145.4(5)	145.0(14)
$p4$: C-Cl	171.7(3)	171.8(3)	171.3(3)
$p5$: C1=C2-C3	124.7(4)	125.1(3)	125.0(7)
$p6$: C3-C2-H5	115(2)	116(2)	112(4)
$p7$: C2=C1-C17	123.7(3)	123.7(2)	123.2(4)
$p8$: C2=C1-H6	124.2(17)	124.5(13)	122(3)
$p9$: φ_1^b	[180]	[180]	[180]
$p10$: φ_2^b	[60]	[60]	59(12)
$p11$: α_2^b	0.04(3)	0.05(3)	0.10(4)
$R(\text{long})^c$	5.53	4.76	5.85
$R(\text{short})^c$	7.02	10.50	9.94
$R(\text{total})^c$	6.25	7.27	7.84

^aValues in parentheses are estimated standard deviations (σ) accounting for data correlation ($\sigma=2\sigma_{LS}$) and, for distances, the uncertainties in the s scale (0.1%). Quantities in brackets were fixed according to results of previous refinements. ^b φ are torsional angles (C=C-C=C) for conformer 1 and 2; α_2 is the mole fraction of conformer 2 ($\alpha_1 = 1 - \alpha_2$). ^c $R = [\sum w_i \Delta_i^2 / \sum w_i / (i(\text{obs})^2)]^{1/2}$ where $\Delta_i = |i(\text{obs}) - i(\text{calc})|$, in %.

verted to the geometrically inconsistent set of r_a distances (Table 3) to be entered in the electron diffraction intensity expression²⁴ by $r_a = r_a - D$ where $D = l/r - K - \delta r$.³² The l and K values (perpendicular amplitude correction coefficient) are those obtained from the normal coordinate calculations using Hilderbrandts computer program.³³ This program also computes the centrifugal stretching of the distances,³² δr , and their magnitudes as compared to the computed K values show that they should not be neglected in the r_a to r_a conversion. Calculated l and D values are given in Table 4, for all three temperatures. For the torsion independent distances, D values for the *anti* form were used.

The r_a model is not entirely satisfactory for molecules with large amplitude motions. In the described dynamic geometrical model, the large amplitude torsional motion about the central C-C bond is separated from the framework structure of the molecule. The vibrational amplitude quantities (l and D values) are then framework values. In the force field calculations, they were obtained by neglecting the contributions from this torsional normal mode. In this treatment, $\varphi_1 = 180^\circ$ and δ is a geometrical parameter which may be determined from the GED data. It gives information about the torsional force constant³⁰ ($f = RT/\delta^2$) and thereby the corresponding normal frequency which is often missing or uncertain in the spectroscopic data.

Structure refinements. The initial structure analysis based on data set B (314 K), showed that it was consistent with a prevailing *anti* conformation of CC2. However, subsequent analysis showed that the presence of small amounts of a second conformer could not be ruled out. In this context, the torsion-dependent interatomic distances C17...C110 and C1...C110 are of principal interest. For the *anti* form, they gave rise to peaks in the RD curve at about 565 and 465 pm (Y and V, respectively in Fig. 3). The one-conformer interpretation gave a slight area surplus for the corresponding theoretical peaks, and there was a more pronounced lack of contribution to the RD curve at about 320 pm. Careful examination of the torsion dependency of $r(\text{C17...C110})$ and $r(\text{C1...C110})$ revealed that they would both give rise to RD contributions in the 320 pm region for φ values about 50–60°. Several grid type refinements yielded a best fit to the data for a conformational mixture containing 5% of a

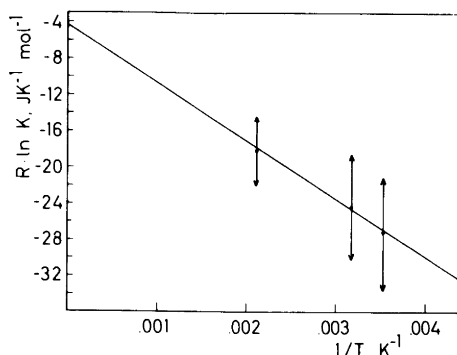


Fig. 4. van't Hoff plot for gaseous *cis,cis*-1,4-dichloro-1,3-butadiene. $K = \alpha_g/\alpha_a$.

gauche form with $\varphi_2 = 55^\circ$. Subsequently, high temperature data were recorded, and the presence of the second form was also demonstrated by the temperature dependency of the V and Y peaks (Fig. 3) which indicated decreased contribution from the *anti* form at the highest temperature. Note that the intermediate curve (314 K, Fig. 3) has higher resolution due to more extended data range than the two others which, except for the temperature difference, are based on identical experimental and calculational conditions.

The structure refinement was then carried out based on the two-conformer interpretation of the data. However, φ_2 (Table 2) was refined only for the highest temperature (set C) which had the largest abundance of the second conformer. As determined in these refinements, $\varphi_2 = 60^\circ$ was used for refinements of set A and B. Neglect of shrinkage corrections gave an apparent deviation from $\varphi_1 = 180^\circ$ for the *anti* form ($\varphi_1 = 167^\circ$, set B), but implementation of the r_a model yielded φ_1 values very close to 180° ; $\varphi_1 = 180^\circ$ was therefore used in the final refinements of the r_a model for all three temperatures (Table 2). The result, $\varphi_a \approx 180^\circ$, suggests that the r_a model and the spectroscopically derived D values account satisfactorily for the shrinkage and that the equilibrium value for φ_1 is indeed 180° . Some l values were also refined individually or in groups as specified in Table 3 which, together with Table 2, contain the final structural results for CC2 at all three temperatures. The corresponding least-squares standard deviations and elements of the correlation matrices are given in Table 5. The

Table 3. Distances (r_a) and amplitudes (l) in *cis,cis*-1,4-dichloro-1,3-butadiene corresponding to results of Table 2.* All quantities in pm.

Distances	Multi- plicity	A: 283 K		B: 314 K		C: 473 K	
		r	l^a	r	l^a	r	l^a
A: C1-H6	2	108.7(7)	8.6(6)	110.4(7)	7.5(5)	108.8(8)	7.7(7)
B: C1=C2	2	134.6(3)	4.1(7)	134.3(2)	3.9(3)	134.9(4)	4.7(12)
C: C2-C3	1	146.1(8)	4.4(B)	145.6(4)	4.1(B)	145.0(14)	4.9(B)
D: C1-C17	2	172.8(3)	5.4(2)	173.1(3)	4.9(2)	173.2(3)	5.8(3)
E: C2-H5	2	108.8(7)	8.7(A)	110.6(7)	7.6(A)	109.0(8)	7.8(A)
F: C2-H6	2	215(2)	11.5(12)	216.1(14)	8.9(10)	213(3)	9.8(14)
G: C3-H6	2	347(17)	-	349.1(12)	-	346(3)	-
H: C1-C3	2	248.2(6)	6.5(8)	348.0(5)	5.6(4)	247.9(9)	7.9(10)
I: H6-C17	2	236(3)	11.1(H)	237(2)	10.2(H)	238(3)	12.3(H)
J: H5-H6	2	250(4)	-	249(5)	-	251(5)	-
K: C1-H5	2	211(3)	11.7(F)	211(3)	9.1(F)	214(4)	10.0(F)
L: C2-C17	2	271.6(6)	6.7(3)	271.6(5)	6.1(2)	272.6(7)	7.4(4)
M: C3-H5	2	215(3)	12.5(F)	217(3)	10.0(F)	211(5)	11.1(F)
N: C3-C17	2	314.1(6)	11.0(4)	314.6(6)	10.0(3)	313.6(9)	14.1(8)
O: H5-C17	2	371(2)	9.9(9)	371(2)	9.5(8)	372(3)	9.6(12)
P1: H6-H9	1	558(4)	-	561(3)	-	554(5)	-
Q1: C1-H9	2	461(2)	-	462.5(18)	-	459(3)	-
R1: C1-C4	1	370.7(9)	7.1(O)	370.3(8)	6.7(O)	370.4(11)	7.2(O)
S1: H6-H8	2	376(5)	-	380(5)	-	371(8)	-
T1: H6-C110	2	511(3)	-	512(2)	-	507(4)	-
U1: C1-H8	2	268(5)	-	271(4)	-	264(7)	-
V1: C1-C110	2	446.9(7)	11.7(6)	446.9(7)	10.8(6)	445.6(10)	14.7(10)
W1: H5-H8	1	307(4)	-	311(4)	-	302(7)	-
X1: H5-C110	2	269(5)	19.9(L)	271(5)	20.0(L)	264(7)	23.5(L)
Y1: C17-C110	1	566.1(9)	11.8(5)	566.4(9)	11.0(5)	564(12)	14.9(9)
P2: H6-H9	1	525(2)	-	529.9(19)	-	525(4)	-
Q2: C1-H9	2	421.5(19)	-	423.7(14)	-	421(5)	-
R2: C1-C4	1	318.8(13)	-	319.5(10)	-	319(7)	-
S2: H6-H8	2	416(4)	-	420(4)	-	411(9)	-
T2: H6-C110	2	417.0(17)	-	420.1(15)	-	416(12)	-
U2: C1-H8	2	322(3)	-	324(3)	-	319(8)	-
V2: C1-C110	2	334.1(13)	-	335.5(16)	-	333(16)	-
W2: H5-H8	1	257(7)	-	262(7)	-	249(13)	-
X2: H5-C110	2	386.9(18)	-	388.9(14)	-	385(14)	-
Y2: C17-C110	1	319.3(13)	-	320.5(11)	-	314(45)	-

*Numbers in parentheses are estimated standard deviations (σ) accounting for data correlation ($\sigma = 2\sigma_{LS}$) and, for the distances, the uncertainty in the s scale (0.1 %); Letters in parentheses for the l values identify the tied l values in grouped refinements; Omitted l values signify that the parameter has been fixed at the calculated value (see Table 4).

least-squares agreement factors (R values) are included in Table 2, and the fit to the experimental data is further illustrated by the difference intensities and difference RD curves shown in Figs. 2 and 3, respectively. It should be noted that the high temperature structure was obtained with one more variable (φ_2) than the two others.

The dynamic model was also tested for set B. It did not give an improved fit to the data. The δ value obtained, $11.4 (10)^\circ$, corresponds to a torsional force constant of $f_t = 0.11 \text{ aJ rad}^{-2}$ as compared to the value of 0.13 aJ rad^{-2} derived from spectroscopic data. Again, good correspondence between spectroscopic and electron diffraction

Table 4. Vibrational amplitude quantities for *cis,cis*-1,4-dichloro-1,3-butadiene at three temperatures ($\ell(T)$ and $d(T)$) calculated from a valence force field (see text). All quantities in pm.

Distances	$\ell(283)$	$d(283)$	$\ell(314)$	$d(314)$	$\ell(473)$	$d(473)$
A: C1-H6	7.7	-1.4	7.7	-1.4	7.7	-1.7
B: C1=C2	4.4	-0.7	4.4	-0.8	4.5	-1.2
C: C2-C3	4.6	-0.2	4.7	-0.2	4.8	-0.3
D: C1-Cl7	4.7	-1.2	4.8	-1.3	5.1	-1.9
E: C2-H5	7.7	-1.5	7.7	-1.6	7.7	-1.9
F: C2-H6	9.5	-1.1	9.5	-1.2	9.6	-1.6
G: C3-H6	9.6	-0.7	9.6	-0.8	9.9	-1.1
H: C1-C3	6.4	-0.4	6.5	-0.4	7.2	-0.6
I: H6-Cl7	11.1	-1.2	11.1	-1.3	11.6	-1.9
J: H5-H6	15.4	-1.1	15.4	-1.2	15.8	-1.8
K: C1-H5	9.7	-1.4	9.7	-1.5	9.8	-2.2
L: C2-Cl7	5.9	-1.6	6.0	-1.8	6.8	-2.7
M: C3-H5	10.5	-0.6	10.6	-0.6	10.9	-0.8
N: C3-Cl7	10.9	-1.1	11.4	-1.3	13.6	-1.9
O: H5-Cl7	9.5	-2.1	9.6	-2.3	10.0	-3.3
P1: H6-H9	12.7	-0.3	12.8	-0.4	13.1	-0.5
Q1: C1-H9	10.7	-0.3	10.7	-0.3	11.3	-0.4
R1: C1-C4	6.7	-0.1	6.8	-0.1	7.5	-0.2
S1: H6-H8	15.9	-0.8	16.2	-0.8	17.3	-1.1
T1: H6-Cl10	17.3	-0.2	17.8	-0.2	20.6	-0.3
U1: C1-H8	14.4	-0.5	14.6	-0.5	15.9	-0.8
V1: C1-Cl10	11.5	-0.3	11.9	-0.3	14.4	-0.5
W1: H5-H8	12.7	-0.8	12.8	-0.9	13.0	-1.1
X1: H5-Cl10	19.1	-1.6	19.7	-1.7	22.9	-2.6
Y1: Cl7-Cl10	10.7	-0.0	11.1	-0.0	13.5	-0.1
P2: H6-H9	14.9	-1.7	15.1	-1.9	16.7	-2.7
Q2: C1-H9	13.4	-1.6	13.8	-1.7	15.7	-2.5
R2: C1-C4	11.4	-1.1	11.9	-1.3	14.1	-1.9
S2: H6-H8	14.8	-0.6	15.0	-0.6	15.8	-0.8
T2: H6-Cl10	23.5	-2.0	24.5	-2.2	29.2	-3.2
U2: C1-H8	12.5	-0.1	12.7	-0.1	13.8	-0.1
V2: C1-Cl10	21.1	-1.9	22.1	-2.1	27.0	-3.2
W2: H5-H8	17.7	-1.4	17.9	-1.5	19.3	-2.3
X2: H5-Cl10	18.7	+0.5	19.3	+0.6	22.5	+0.9
Y2: Cl7-Cl10	42.6	+0.4	44.8	+0.4	55.1	+0.6

information about the vibrational properties of CC2 was indicated for data set B. Comparisons of refined and spectroscopic l values (Tables 3 and 4) also support this notion. The dynamic model description applied on data sets A and C, however, yielded δ values of 14.2 (9) and 18.7 (13) $^\circ$ corresponding to f_t values of 0.06 and 0.07 aJ rad $^{-2}$, respectively for the low and high temperatures. This may be related to the fact that these data were obtained with a low pressure nozzle, 21 but also for a more limited data range (Table 1).

Conformational composition and thermodynamic quantities. The temperature variation of the composition parameter (α_2 , Table 2) contains information about the thermodynamic quantities for the gas phase *anti* \rightleftharpoons *gauche* equilibrium for CC2: 30,35 $K = \alpha_g/\alpha_a = 2 \exp(\Delta S_c^\circ/R) \cdot \exp(-\Delta E^\circ/RT)$ or $R \ln K = \Delta S_c^\circ + R \ln 2 - \Delta E^\circ/T$ where α_g and α_a are the mole fractions of the two conformers ($\alpha_2 = \alpha_g$) and the factor 2 is the ratio of the statistical weights of the *gauche* and the *anti* form. The entropy difference where the statistical weight has been removed from the *gauche*

Table 5. Least-squares standard deviations, $\sigma_i(\text{LS})$, for the structure parameters (p , φ , α , Table 2), amplitude parameters (1, Table 3) and the scale factors (S); and elements of the correlation matrices, ρ_{ij} , with values $|\rho_{ij}| > 0.60$. A, B, and C refer to the three refinements of Tables 2 and 3.

i :	$\sigma_i(\text{LS})$			j :	$100 \times \rho_{ij}$ (A, B, C)
	A	B	C		
$p1$	0.3	0.3	0.4		
$p2$	0.10	0.07	0.17		
$p3$	0.4	0.17	0.6	$p2$:	-78(C)
$p4$	0.06	0.04	0.07		
$p5$	0.2	0.14	0.3	$p3$:	-66(A), -62(B), -68(C);
$p6$	1.1	1.1	1.8		
$p7$	0.14	0.09	0.2	$p2$:	-68(C); $p3$: +66(C); $p5$: -85(A), -85(C)
$p8$	0.9	0.7	1.4	$p5$:	+70(C); $p7$: -60(A), -64(C)
$\varphi2$	-	-	0.6		
ℓA	0.3	0.3	0.3		
ℓB	0.4	0.15	0.5	$p2$:	+77(C); $p3$: -86(A), -92(C); $p7$: -61(C)
ℓD	0.12	0.08	0.15		
ℓF	0.6	0.5	0.7		
ℓH	0.4	0.2	0.5	$p6$:	-60(A), -63(C); $p8$: -62(A), -70(C)
ℓL	0.14	0.10	0.19		
ℓN	0.19	0.17	0.40		
ℓO	0.4	0.4	0.6		
ℓV	0.3	0.3	0.5		
ℓY	0.3	0.2	0.4		
$\alpha2$	1.3	1.7	2.0		
$S(l)$	0.8	0.7	1.6	$p1$:	-62(C); ℓD : +67(A), +64(B), +70(C)
$S(\text{sh})$	1.1	1.3	1.9	ℓD :	+80(A), +72(B), +81(C); $S(l)$: +67(A), +69(C)

form, $\Delta S_c^\circ = S_g^\circ - S_a^\circ$, and the energy difference, $\Delta E^\circ = \Delta H^\circ = E_g^\circ - E_a^\circ$, were determined from an Arrhenius plot of the composition data (Fig. 4): $\Delta S_c^\circ + R \ln 2 = 4.5 \text{ J K}^{-1} \text{ mol}^{-1}$, $\Delta S_c^\circ = -11 \text{ (15) J K}^{-1} \text{ mol}^{-1}$, and $\Delta E^\circ = \Delta H^\circ = 6 \text{ (5) kJ mol}^{-1}$. The large standard deviations reflect the large uncertainties in the determination of the composition parameter (α_2 , Table 2).

Discussion

The presence of a *gauche* form in addition to the predominating *anti* form in gaseous of CC2 as indicated by GED data for 314 K has been supported by the interpretation of two new data sets (283 and 473 K). The *gauche* abundance (α_2 , Table 2) is low in all three cases and it is not determined with high accuracy. However, the conclusion is confirmed by the additional evidence contained in the temperature dependence of the composition as illustrated clearly by the RD curves (Fig. 3). Taking into account the high stan-

dard deviations for the α_2 parameters (Table 2) and also a possibility of overestimating some vibrational amplitude parameters (see below) for the two additional sets of data (283 and 473 K), it is remarkable that the $R \ln K$ data versus T^{-1} conform closely to linearity (Fig. 5). This may be fortuitous, but it allows for evaluation of ΔH° and ΔS° for the *anti* \rightleftharpoons *gauche* equilibrium. The energy difference, $\Delta E^\circ = 6 \text{ (5) kJ mol}^{-1}$, appears to be similar to the values of 9.2 (46) and 5.8 (15) kJ mol $^{-1}$ obtained for the corresponding conformational equilibria for 2,3-dichloro-1,3-butadiene¹⁶ and oxalyl chloride,³⁰ respectively. These two molecules have entropy differences of -4.3 (92) and 9.6 (42) J K $^{-1}$ mol $^{-1}$, when the entropy of mixing ($R \ln 2$) is removed, as compared to -11 (15) J K $^{-1}$ mol $^{-1}$ for CC2. Steric interactions, which may reduce the freedom of internal motion, are probably important for the *gauche* form of CC2 which, due to such effects, cannot assume a planar *syn* conformation. It is clear from the interpretation of the RD curve that the C17...C110

Table 6. Comparison of the molecular structures^a of some gaseous 1,3-butadienes. Distances in pm, angles in degrees.

	1,3-butadiene ³	2,3-dichloro-1,3-butadiene ¹⁶	<i>cis,cis</i> -1,4-dichloro-1,3-butadiene ^b	hexachloro-1,3-butadiene ³⁹
C-H	109.0(4)	110.3(5)	110.5(7)	—
C=C	134.1(2)	133.7(2)	134.3(2)	134.9(6)
C-C	146.3(3)	147.2(4)	145.6(4)	148.3(18)
C-Cl	—	174.5(2)	173.1(3)	171.5(2)
C=C-C	123.3(3)	126.1(3)	125.1(3)	123.4(6)
C-C-X	114(3)	115.2(3)	116(2)	114.6(7)
C=C1-X _t	120(2)	} 118.7(15)	124.5(13)	122.5(2)
C=C1-X _c	120(2)		123.7(2)	
φ ₁	180.0	180.0	180.0	78.1(11)
φ ₂	—	52.0	60.0	—

^aX refers to H or Cl; subscripts *t* and *c* for the terminal substituents refer to *trans* and *cis* with respect to the C=C-C angle. ^bPresent work.

distance of the second form should contribute to the area about 320 pm. The low abundancy of this form together with the large amplitudes of vibration associated with its Cl7...Cl10 and C1...Cl10 distances (Table 3) make determination of the torsional angle difficult. It is, however, found to be about 60° which, in fact, corresponds to a staggered conformation in the bent bond description of the double bond. The corresponding average Cl...Cl distance for the three temperatures (Table 3) is 318 pm as compared to values of 327 and 319 pm found for the Cl...Cl distances in 2,3-dichloro-1,3-butadiene¹⁶ and oxalyl chloride³⁰ which have torsional angles of 52 (10)° and 55 (6)° for the less abundant conformer. Thus, these compounds have Cl...Cl interactions substantially shorter than the van der Waals distance of about 360 pm.³⁶ Such effects, although not so pronounced, have been discussed for 2,2'-dichloro biphenyl^{40,37} which has only one conformation with φ(C-C) = 74° and r(Cl...Cl) = 346 pm.³⁸

The experimentally determined bond distances and valence angles are essentially those of the *anti* form, particularly for the lower temperatures. There are no changes in these parameters (Table 2) which can be ascribed to temperature effects. This may indicate that the assumption of equal framework structures for the two forms is valid, but also that any difference is not observable due to the low contribution of the *gauche* form. Several refined amplitude parameters do

vary as a function of the temperature (Table 3), which is expected from the trends established by the results (Table 4) of the force field calculation (*l*(calc)). However, it appears that, as compared to the *l*(calc) values, the refined amplitudes (*l*(GED)) are slightly larger for refinements A and C, than for B. The deviation from a consistent temperature dependence for the vibrational amplitude parameters is most clearly reflected in the large values obtained for the δ parameter for data sets A and C, as compared to the expected value based on spectroscopic data and the result of refinement B. Results of careful studies of gaseous benzene, using conventional and different types of low pressure nozzles, show that *l*(GED) > *l*(calc) for nonbonded interactions.²² Thus, it appears that the use of low pressure nozzles may introduce discrepancies between results obtained by gas phase electron diffraction and spectroscopy. In addition, data sets A and C have a reduced data range and we have chosen to present our final structural results for CC2 as those obtained in refinement B (314 K) rather than as an averaged structure based on all three sets of results. The distance parameters of Table 2 are converted from *r_a* type values to *r_s* type values (see Table 3) and the structural results for CC2 are compared with the GED structures of 1,3-butadiene and two chloro-substituted 1,3-butadienes in Table 6. Further comments on the results will be made in forthcoming papers on GED investigations of the two isomeric compounds 1,4-di-

chloro-1,3-butadiene (*cis,trans* and *trans,trans*)⁴⁰ and on *trans,trans*-1,2,3,4-tetrachloro-1,3-butadiene.⁴¹

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