

# The Molecular Structures of the *anti* Conformers of *trans,trans*-1,4-Dichloro-1,3-butadiene and *cis,trans*-1,4-Dichloro-1,3-butadiene Determined by Gas-Phase Electron Diffraction

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Gundersen, G., Smith, Z. and Thomassen, H., 1988. The Molecular Structures of the *anti* Conformers of *trans,trans*-1,4-Dichloro-1,3-butadiene and *cis,trans*-1,4-Dichloro-1,3-butadiene Determined by Gas-Phase Electron Diffraction. – Acta Chem. Scand., Ser. A 42: 477–492.

The electron-diffraction data for the vapours of the title compounds at about 310 K have been interpreted in terms of prevailing *anti* conformations ( $\varphi = 180^\circ$ ) for both compounds. Principal bond distances ( $r_a$ ) and valence angles ( $\angle_a$ ) are: for *trans,trans*-1,4-dichloro-1,3-butadiene,  $r(\text{C}=\text{C}) = 134.1(2)$ ,  $r(\text{C}-\text{C}) = 145.2(5)$ ,  $r(\text{C}-\text{Cl}) = 172.4(2)$  pm,  $\angle(\text{C}=\text{C}-\text{C}) = 121.9(6)$ ,  $\angle(\text{C}=\text{C}-\text{Cl}) = 122.7(3)^\circ$ ; for *cis,trans*-1,4-dichloro-1,3-butadiene,  $r(\text{C}-\text{H}) = 109.5(6)$ ,  $r(\text{C}=\text{C}) = 134.1(2)$ ,  $r(\text{C}-\text{C}) = 145.6(4)$ ,  $r(\text{C}-\text{Cl}) = 172.3(2)$  pm,  $\angle(\text{C}=\text{C}-\text{C})_{\text{cis}} = 125.6(6)$ ,  $\angle(\text{C}=\text{C}-\text{C})_{\text{trans}} = 122.0(6)$ ,  $\angle(\text{C}=\text{C}-\text{Cl})_{\text{cis}} = 123.9(3)$ ,  $\angle(\text{C}=\text{C}-\text{Cl})_{\text{trans}} = 122.9(4)^\circ$ .

The presence of about 5% of *synclinal* conformers with apparent torsion angles of about  $50^\circ$  at 310 K could not be ruled out. Analyses of 473 K data (of poor quality) confirmed the presence of 15(3)% of the second form for the *trans,trans* isomer, whereas conflicting results were obtained for the *cis,trans* isomer.

Dedicated to Professor Otto Bastiansen on his 70th birthday

Vibrational spectroscopic data for the three isomers of 1,4-dichloro-1,3-butadiene have shown that these molecules exist predominantly in the *anti* conformation [ $\varphi(\text{C}=\text{C}-\text{C}) = 180^\circ$ ],<sup>1,2</sup> as does the parent molecule, 1,3-butadiene. The molecular structure of *anti* 1,3-butadiene has been determined by gas-phase electron diffraction (GED)<sup>3</sup> and in a previous paper we have reported the gas-phase molecular structure of *anti cis, cis*-1,4-dichloro-1,3-butadiene (hereafter referred to as CC2) as determined by GED.<sup>4</sup> The molecular structures of some other chloro-derivatives of 1,3-butadiene for which the *anti* conformers are prevalent in the gas phase have also been reported: the 2,3-dichloro compound (referred to as D23) by GED<sup>5</sup> and the *cis*-1-chloro,<sup>6</sup> *trans*-1-chloro<sup>7</sup> and 2-chloro<sup>8</sup> derivatives by MW spec-

troscopy. Rather large structural substitution effects were reported and discussed for the two 1-chloro compounds.<sup>6,7</sup> Comparable effects were not observed by GED for CC2.<sup>4</sup> We now report the results of analogous GED studies of *trans,trans*- and *cis,trans*-1,4-dichloro-1,3-butadiene, hereafter referred to as TT2 and CT2, respectively. The aim of the present paper is primarily to give further information about the gas-phase structures of the prevalent conformers of chloro-substituted 1,3-butadienes.

Another interesting aspect of structure studies of these compounds is, however, the possible presence of minor conformers in the gas phase. In fact, the nature of the minor conformer of the parent molecule, 1,3-butadiene, has been controversial for a long time, as summarized in our previous paper.<sup>4</sup> It appears that the second conformer (about 11–14 kJ mol<sup>-1</sup> higher in energy

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than the planar *anti* conformer) is *nonplanar syn* ( $\varphi = 20\text{--}40^\circ$ ) with a low barrier to *planar syn* ( $\varphi = 0^\circ$ ). However, the opinion that  $C_{2v}$  symmetry ( $\varphi = 0^\circ$ ) actually represents the second potential energy minimum persists,<sup>9</sup> and it has been argued that the *syn* barrier predicted by SCF calculations may disappear when electron correlation is included.<sup>10</sup> An early high-temperature GED study suggested *gauche* to be the less abundant conformer of 1,3-butadiene, although conclusive evidence was never published.<sup>11</sup> A stable *gauche* form ( $\varphi = 52^\circ$ ) 9.2(46) kJ mol<sup>-1</sup> higher in energy than planar *anti* is identified by GED for D23,<sup>5</sup> and the presence of 4(3) to 10(4) % of a *gauche* form ( $\varphi = 60^\circ$ ) at 283 to 473 K for CC2<sup>4</sup> corresponds to a *gauche-anti* energy difference of 6(5) kJ mol<sup>-1</sup>. Inspection of models shows that the conformational angles of the minor *syn* conformer of CC2 and D23 could be governed by Cl...Cl nonbonded interactions which prohibit planar *syn* conformations ( $\varphi = 0^\circ$ ). For the title compounds the close "7...10" and "5...6" interactions in the *syn* forms (cf. Fig. 1) do not involve Cl...Cl, but H...H for TT2 and Cl...H and H...H for CT2. It thus appears that planar *syn* is sterically allowed for TT2 which in this respect is similar to 1,3-butadiene. *Synperiplanar* conformations ( $\varphi < 30^\circ$ ) of CT2 could, however, be prohibited by close Cl...H interactions as  $\varphi$ -values of 45 to 60° would be required to give C17...H10 (cf. Fig. 1) a length similar to the van der Waals distance of 270–310 pm and, for example, similar to the close Cl...H distance for planar *anti* for CC2 [269(5) pm] and D23 [262(5) pm]. Experimental characterizations of any minor conformers of TT2 and CT2 would therefore be of interest, and the remainders of the TT2 and CT2 samples were used to record data at higher temperatures. It should be noted that the identification of the second form of CC2 was marginal, the abundance being only 10% at 473 K, which is the upper temperature limit for these compounds with our present equipment. However, only brief accounts of the conformational analyses of TT2 and CT2 are included in the present paper as these, being hampered by poor high-temperature data, gave less conclusive results than for CC2.

Conformational predictions may also be obtained from molecular mechanics (MM) calculations. We employed an approach which was said to reproduce all trends in conformational energies, barrier heights, structural parameters and

torsional force constants of stable conformers simultaneously for halogenated propenes, 1,3-butadienes and biphenyls,<sup>12</sup> and for a number of chloro derivatives of 1,3-butadiene.<sup>13</sup> As described elsewhere, we agree that experimental findings were reproduced fairly well for the nonplanar hexachloro- and *trans,trans*-1,2,3,4-tetrachloro-1,3-butadiene,<sup>14</sup> but several of the other predictions seem to be unreasonable. In addition, recalculations on 1,3-butadiene and D23, studies of which were included in the original paper,<sup>12</sup> revealed that the published results for these two molecules are inconsistent with the recommended set of potential parameters and structure reference values: Firstly, the *syn-anti* energy difference for 1,3-butadiene is calculated as 4.6 kJ mol<sup>-1</sup> rather than 9.6 kJ mol<sup>-1</sup> as claimed, and consequently it is rather low compared to other predictions of 11–14 kJ mol<sup>-1</sup>. Secondly, the published energy curves for D23<sup>12</sup> obtained with and without excess charges on the atoms were different, as only the latter had a second energy minimum at  $\varphi = 50^\circ$ , about 13 kJ mol<sup>-1</sup> above *anti*. Our calculations, however, failed in all cases to reproduce a second minimum, and at  $\varphi = 50^\circ$  the energy was about 30 kJ mol<sup>-1</sup> above that for *anti*, as compared to the experimental value<sup>5</sup> of 9.2 kJ mol<sup>-1</sup>. Consequently, further interpretations of results obtained by this method were abandoned.

### Experimental and data processing

Samples of the three isomeric 1,4-dichloro-1,3-butadienes (CC2, TT2 and CT2) obtained as described previously<sup>2</sup> were used for both spectroscopic<sup>2</sup> and GED studies. The chromatographic separation of the three isomers was tedious and it was most difficult to obtain quantities of pure TT2. Two batches of TT2 were used in the investigations. Analysis of the spectroscopic data for TT2 showed that small amounts of CT2 could be present in the first sample used to obtain data at 310 K, whereas gas chromatographic analyses of a small residue left after the very last GED experiment indicated a purity of at least 99 %.

GED diagrams were recorded for TT2 and CT2 at three temperatures using two different nozzle systems. Experimental details are given in Table 1. It should be noted that the doughnut-shaped low-pressure nozzle used to obtain data sets A and C appears to affect the determination

Table 1. Experimental conditions for *trans,trans*- and *cis,trans*-1,4-dichloro-1,3-butadiene (TT2 and CT2, respectively).

	Data set (nozzle temperature)					
	A (283 K)		B (310 K)		C (473 K)	
Nozzle-to-plate distance/mm	484.78	334.78	477.68	197.68	484.78	334.78
Electron wavelength/pm	6.466	6.466	6.470	6.470	6.466	6.466
No. of plates <sup>a</sup> TT2:	3×2	(3×2)	4	4	3×2	(3×2)
CT2:	–	4	5	6	3×2	5
Data range						
$s_{\min}/\text{nm}^{-1}$	20.0	40.0	20.0	80.0	20.0	40.0
$s_{\max}/\text{nm}^{-1}$	180.0	270.0	197.5	390.0	180.0	270.0
$\Delta s/\text{nm}^{-1}$	1.25	2.5	1.25	2.5	1.25	2.5
Data weighting <sup>b</sup>						
$s_1/\text{nm}^{-1}$	50.0	50.0	50.0	80.0	50.0	50.0
$s_2/\text{nm}^{-1}$	120.0	150.0	197.5	250.0	120.0	150.0
$w_1/10^{-4} \text{ nm}^2$	15	15	15	0	15	15
$w_2/10^{-4} \text{ nm}^2$	23	1	0	1	23	1

<sup>a</sup>Parentheses signify that analyses of these plates were ultimately abandoned due to high noise-to-signal ratios; ×2 that these plates were subjected twice to photometry. <sup>b</sup>See Ref. 4 for further comments on data weighting.

of vibrational amplitude parameters as discussed in the CC2-study.<sup>4</sup> In addition the data ranges were reduced in these experiments (cf. Table 1) due to sample limitations. Finally, we failed to obtain usable long-camera data for CT2 at 283 K, and other parts of data sets A and C were of poor quality as specified in Table 1. The 283 K and 473 K data were nevertheless analysed in an attempt to obtain some preliminary information about the conformational compositions of the gases. However, the structure determinations of the prevalent conformer are based upon the 310 K data (B) which were obtained concurrently with the spectroscopic work<sup>2</sup> using a conventional nozzle.

Densitometry of the electron-diffraction diagrams, data reduction to the  $s/|f_c|/|f_{cl}|$ -modified molecular intensities and the analysis procedure for TT2 and CT2 were as described in our previous GED study of CC2.<sup>4</sup>

The weighting of the data in the least-squares refinement procedures was as specified in Table 1. The experimental molecular intensity curves for data sets B are shown in Figs. 2 and 3 for TT2 and CT2, respectively. Experimental radial distribution curves (RD curves) are shown in Figs. 4 and 5 for TT2 and Figs. 6 and 7 for CT2.

## Structure analyses

*Geometrical models and corrections for vibrational effects.* Perspective views of the planar *anti* forms ( $\varphi = 180^\circ$ ) and a nonplanar *syn* form ( $\varphi = 30^\circ$ ) of the TT2 and CT2 molecules are shown in Fig. 1. The geometries of the two molecules were specified by the  $r_\alpha$ -type parameters defined in Table 2. The vibrational corrections ( $D = r_\alpha - r_a$ ) and root-mean-square amplitudes of vibration ( $l$  values) at pertinent temperatures were calculated from the literature force fields<sup>2</sup> as described for CC2.<sup>4</sup> The 310 K values are given in Tables 3 and 4.

A large amplitude model ( $r'_\alpha$ ) was used in addition to the  $r_\alpha$  model in the analysis of the CC2 data,<sup>4</sup> but for two reasons it was not implemented in the present investigations of CT2 and TT2: Firstly, the  $r_\alpha$  model and the dynamic model ( $r'_\alpha$ ) gave consistent results for CC2, suggesting that the former accounts satisfactorily for shrinkage effects. Secondly, the potential energy distribution obtained in the normal coordinate calculations<sup>2</sup> showed that the low-frequency modes were mixed for TT2 and CT2, thus making the separation of the torsional mode-about the central

Table 2.  $r_a$ -type structural results for the *anti* conformers of *trans,trans*-1,4-dichloro-1,3-butadiene (TT2) and *cis,trans*-1,4-dichloro-1,3-butadiene (CT2) obtained from GED data at 310 K compared with analogous results for *cis,cis*-1,4-dichloro-1,3-butadiene (CC2).<sup>a</sup> Values in square brackets for the distances are the  $r_a$  counterparts to the  $r_a$  values.

Parameters	TT2 <sup>b</sup> (This work)	CT2 <sup>c</sup> (This work)	CC2 (Ref. 4)
$r(\text{C}-\text{H})^d$	110.0(8)[111.8]	108.1(6)[109.5]	109.0(7)[110.7]
$r(\text{C}=\text{C})$	133.3(2)[134.1]	133.7(2)[134.1]	133.5(3)[134.3]
$r(\text{C}-\text{C})$	145.9(5)[146.2]	145.4(4)[145.6]	145.4(5)[145.6]
$r(\text{C}-\text{Cl})$	171.5(2)[172.4]	171.9(2)[172.3]	171.8(3)[173.1]
$\angle(\text{C}=\text{C}-\text{C})$	121.9(6)	125.6(4)	125.1(3)
$\Delta(\text{C}=\text{C}-\text{C})$	—	-3.6(5) <sup>c</sup>	—
$\angle(\text{C}3-\text{C}2-\text{H})$	119(2)	119(2)	116(2)
$\angle(\text{C}2=\text{C}1-\text{H})$	125(2)	125.2(12)	124.5(13)
$\angle(\text{C}=\text{C}-\text{Cl})$	122.7(3)	123.9(3)	123.7(2)
$\Delta(\text{C}=\text{C}-\text{Cl})$	—	-1.0(6) <sup>c</sup>	—
$\varphi(\text{C}=\text{C}-\text{C}=\text{C})$	1890 (fixed)	180.0 (fixed)	180 (fixed)
$R$ (long) <sup>e</sup>	5.0	4.8	4.8
$R$ (short)	12.4	10.7	10.5
$R$ (tot)	7.5	6.8	7.3

<sup>a</sup>Distances in pm and angles in degrees. Values in parentheses are estimated standard deviations ( $\sigma$ ) accounting for data correlation ( $\sigma = 2\sigma_{LS}$ ) and for the distances, the uncertainties in the  $s$  scale (0.1%). <sup>b</sup>See text for comments on gas composition; further structural results in Tables 3 and 5. <sup>c</sup>The parameters refer to the *cis* moiety (see text). For *trans*:  $\angle(\text{C}=\text{C}-\text{C}) = 122.0(6)$  and  $\angle(\text{C}=\text{C}-\text{Cl}) = 122.9(4)$ , and  $\Delta r_a$  for bond distances are fixed to give  $r_a$  (*trans*) =  $r_a$  (*cis*). Further structural results in Tables 4 and 6. <sup>d</sup>The various types of C-H distances were assumed to have equal  $r_a$  values giving fixed  $r_a$  (C-H) split parameters (cf. Tables 3 and 4). <sup>e</sup>Least-squares agreement factor in %.

C-C bond from the rest of the molecular dynamics somewhat dubious. In consistency with the results for CC2 we could not detect significant deviations from planarity in the  $r_a$  model of the major *anti* conformations of TT2 and CT2, and ultimately the torsional angles of the *anti* forms ( $\varphi_1$ ) were maintained at 180°, as shown in Table 2.

A two-conformer interpretation of the data was provided by introduction of a composition variable, viz. the mole fraction ( $\alpha_1$ ) of the major conformer, giving  $\alpha_2 = 1.00 - \alpha_1$  for the minor conformer. The torsional angle of the second form ( $\varphi_2$ ) was the only additional geometrical

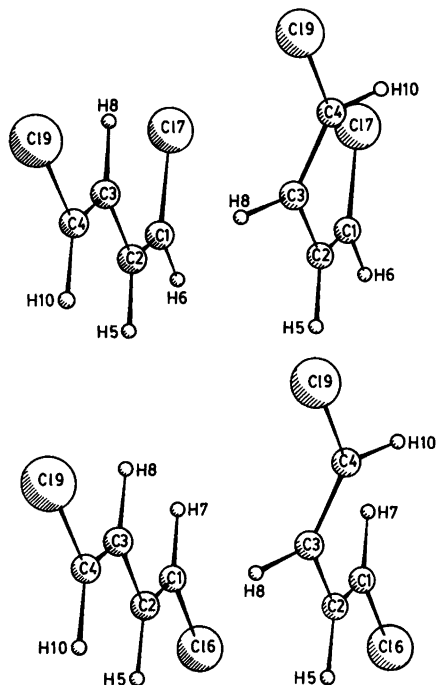


Fig. 1. Perspective views with labelling of the atoms of the *trans,trans* and *cis,trans* isomers of 1,4-dichloro-1,3-butadiene TT2 (lower) and CT2 (upper), respectively. The conformers shown are planar *anti*,  $\varphi = 180^\circ$  (left) and a *syn* form (right) with  $\varphi = 30^\circ$ .

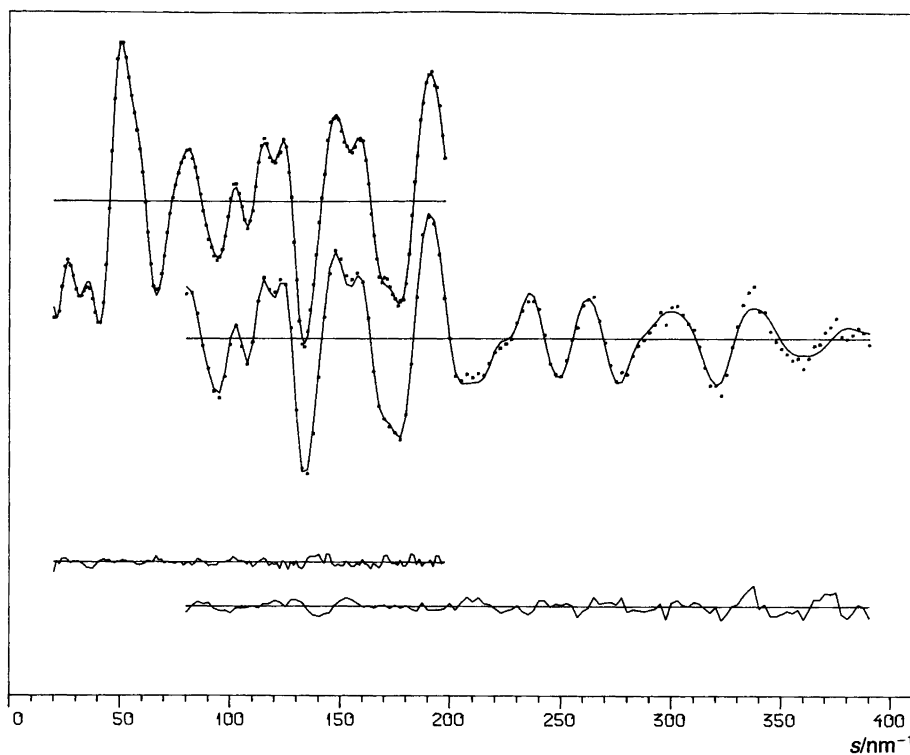


Fig. 2. Observed (●), final theoretical (—) and difference (below) molecular intensity curves for *trans,trans*-1,4-dichloro-1,3-butadiene (TT2) at 310 K.

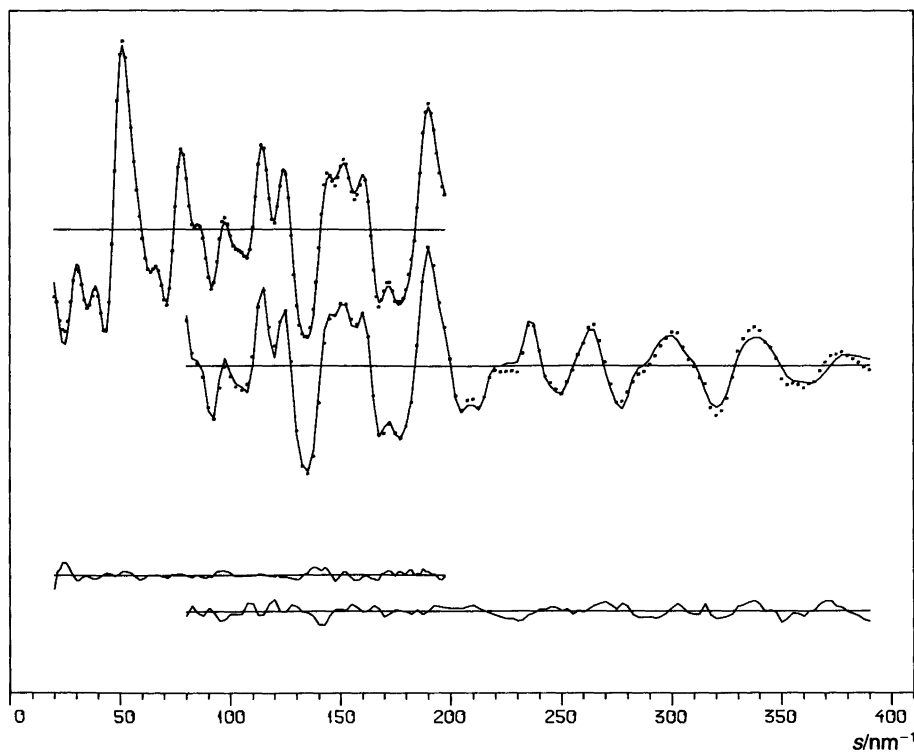


Fig. 3. Observed (●), final theoretical (—) and difference (below) molecular intensity curves for *cis,trans*-1,4-dichloro-1,3-butadiene (CT2) at 310 K.

Table 3. Distances ( $r_a$ ) and amplitudes ( $l$ ) for the interatomic interactions in *trans,trans*-1,4-dichloro-1,3-butadiene (TT2), corresponding to the results of Table 2 and vibrational amplitude quantities ( $l$  and  $D$ ) calculated from a molecular force field. All quantities in pm.

Interactions <sup>a</sup>	Multi- plicity	GED results <sup>b</sup>		Calculated	
		$r_a$	$l$	$l$	$D$
1: C4–H10	2	111.8(8)	8.2(7)	7.68	–1.78
2: C3–H8	2	111.8(8)	8.3 (tied to 1)	7.74	–1.54
3: C3=C4	2	134.1(2)	3.5(4)	4.37	–0.82
4: C2–C3	1	146.2(5)	3.8 (tied to 4)	4.64	–0.32
5: C4–Cl9	2	172.4(2)	4.7(2)	4.71	–0.90
6: C2...C4	2	244.7(5)	6.5(6)	6.50	–0.53
7: C3...Cl9	2	269.3(4)	6.2(3)	6.10	–1.06
8: C2...Cl9	2	405.4(5)	6.3(4)	6.54	–0.71
9: Cl9...H10	2	238.1(7)	10.9 (tied to 6)	10.87	–1.25
10: Cl9...H8	2	285(5)	13.7 (tied to 7)	13.59	–1.19
11: C3...H10	2	217.6(5)	10.3(15)	9.77	–1.89
12: C4...H10	2	212.1(7)	10.1 (tied to 11)	9.60	–1.52
13: C2...H8	2	221.8(9)	11.2 (tied to 11)	10.67	–0.71
14: C2...H10	2	276(2)	–	14.18	–1.02
15: H8...H10	2	314(2)	–	11.99	–2.47
16: C1...C4	1	365.5(8)	7.4(16)	6.72	–0.13
17: C1...Cl9	2	512.5(6)	8.2(5)	8.20	–0.23
18: H5...H10	2	256(3)	–	21.27	–1.48
19: Cl9...H5	2	442(5)	14.6 (tied to 8)	14.88	–0.70
20: Cl9...Cl6	1	671.0(11)	7.8(5)	7.75	0.00
21: H7...H10	1	472(7)	–	16.56	–0.08
22: C4...H5	2	271(4)	–	14.77	–0.81
23: C1...H10	2	408(6)	–	14.12	–0.13
24: Cl6...H10	2	530(5)	17.6 (tied to 17)	17.57	–0.10
25: H5...H8	1	318(4)	–	12.83	–0.79

<sup>a</sup>See Fig. 1 for numbering of atoms. <sup>b</sup>Numbers in parentheses are estimated standard deviations (see comment *a* in Table 2). Omitted  $l$  values signify that the calculated values have been used.

variable used in the specification of the two-conformer situation, as it was assumed that any two conformers would differ geometrically only in the torsional angles. The vibrational amplitude parameters ( $l$  and  $D$  values) associated with the torsion-sensitive distances (ten for TT2 and sixteen for CT2) for the minor form were calculated for appropriate geometries using the force fields established for the *anti* conformers.

The interpretations of the RD curves (Figs. 4 to 7) according to the presence of only one conformer with a torsional angle  $\varphi_1 = 180^\circ$  (i.e. *anti*) are shown by the line diagrams which represent the interatomic distances specified in Tables 3 and 4 for TT2 and CT2, respectively. To aid in

the search for evidence in the RD curves for the presence of any second forms we have examined the variation in torsion angle with the magnitude of selected distances (Fig. 8).

*Refinements and results for TT2.* The experimental RD curve for the 310 K experiment is shown in Fig. 4. It is compared with a theoretical counterpart corresponding to a one-conformer refinement which included the  $l$  values and  $l$  value groups specified in Table 3, giving a least-squares agreement factor of  $R(\text{tot}) = 8.20\%$ . In this interpretation the area discrepancy in the RD curve at the location of the Cl...Cl distance (about 670 pm) is most striking. The immediate response to

Table 4. Distances ( $r_a$ ) and amplitudes ( $I$ ) for the interatomic interactions in *cis,trans*-1,4-dichloro-1,3-butadiene (CT2), corresponding to the results of Table 2 and vibrational amplitude quantities ( $I$  and  $D$ ) calculated from a molecular force field. All quantities in pm.

Interactions <sup>a</sup>	GED results <sup>b</sup>		Calculated	
	$r_a$	$I$	$I$	$D$
1: C1–H6	109.5(6)	8.2(5)	7.68	–1.37
2: C4–H10	109.5(6)	8.2 (tied to $I1$ )	7.68	–2.89
3: C2–H5	109.5(6)	8.2 (tied to $I1$ )	7.74	–1.41
4: C3–H8	109.5(6)	8.2 (tied to $I1$ )	7.74	–3.57
5: C1=C2	134.07(19)	4.0(3)	4.43	–0.34
6: C3=C4	134.07(19)	3.9 (tied to $I5$ )	4.33	–1.12
7: C2–C3	145.6(4)	4.2 (tied to $I5$ )	4.64	–0.18
8: Cl7–C1	172.34(19)	5.10(16)	4.78	–0.49
9: Cl9–C4	172.34(19)	5.02 (tied to $I8$ )	4.70	–0.75
10: C1…C3	248.405)	5.6(6)	6.56	–0.07
11: C2…C4	244.1(3)	5.6 (tied to $I10$ )	6.51	–0.58
12: Cl7…C2	270.9(5)	6.1(2)	5.92	–0.51
13: Cl9…C3	268.5(3)	6.4 (tied to $I12$ )	6.20	–0.28
14: Cl7…C3	315.4(7)	10.2(6)	11.20	–0.17
15: Cl9…C2	404.5(6)	6.4(4)	6.56	–0.22
16: Cl7…H6	234.0(17)	9.1(18)	11.20	–0.66
17: Cl9…H10	235.8(17)	8.6 (tied to $I16$ )	10.71	–2.48
18: Cl7…H5	366.9(20)	9.3(9)	9.51	–0.86
19: Cl9…H8	284(4)	14.0 (tied to $I12$ )	13.80	–1.33
20: C2…H6	215.8(12)	–	9.58	–0.78
21: C3…H10	216.4(12)	–	9.77	–3.37
22: C1…H5	206(3)	–	9.61	–0.92
23: C4…H8	210(3)	–	9.60	–3.64
24: C3…H5	220(3)	–	10.70	–0.50
25: C2…H8	219(3)	–	10.70	–1.60
26: C3…H6	348.9(10)	–	9.67	–0.44
27: C2…H10	276(3)	–	14.21	–2.15
28: H6…H5	244(4)	–	15.58	–0.61
29: H8…H10	310(2)	–	12.00	–5.85
30: C1…C4	368.2(6)	6.5 (tied to $I18$ )	6.76	–0.33
31: Cl7…C4	448.2(7)	11.4 (tied to $I15$ )	11.63	–0.06
32: Cl9…C1	516.5(8)	7.9(7)	8.47	–0.04
33: Cl7…Cl9	558.7(10)	15.1(7)	17.51	0.36
34: H5…H10	256(6)	–	21.38	–1.74
35: Cl7…H8	279(4)	20.0 (tied to $I13$ )	19.80	–1.10
36: Cl9…H5	440(4)	14.6 (tied to $I15$ )	14.81	–0.12
37: Cl9…H6	615.6(12)	10.4(7)	10.68	–0.20
38: Cl7…H10	518.6(18)	13.4 (tied to $I32$ )	13.99	–0.86
39: C1…H8	276(4)	–	14.89	–0.97
40: C4…H5	269(4)	–	14.86	–0.36
41: C4…H6	458.9(19)	–	10.85	–0.45
42: C1…H10	409(2)	–	14.16	–1.34
43: H6…H8	384(4)	–	16.39	–1.10
44: H6…H10	482(4)	–	18.58	–1.10
45: H5…H8	313(4)	–	12.84	–1.70

<sup>a</sup>See Fig. 1 for numbering of atoms. All interactions have multiplicities one. <sup>b</sup>See comment b, Table 3.

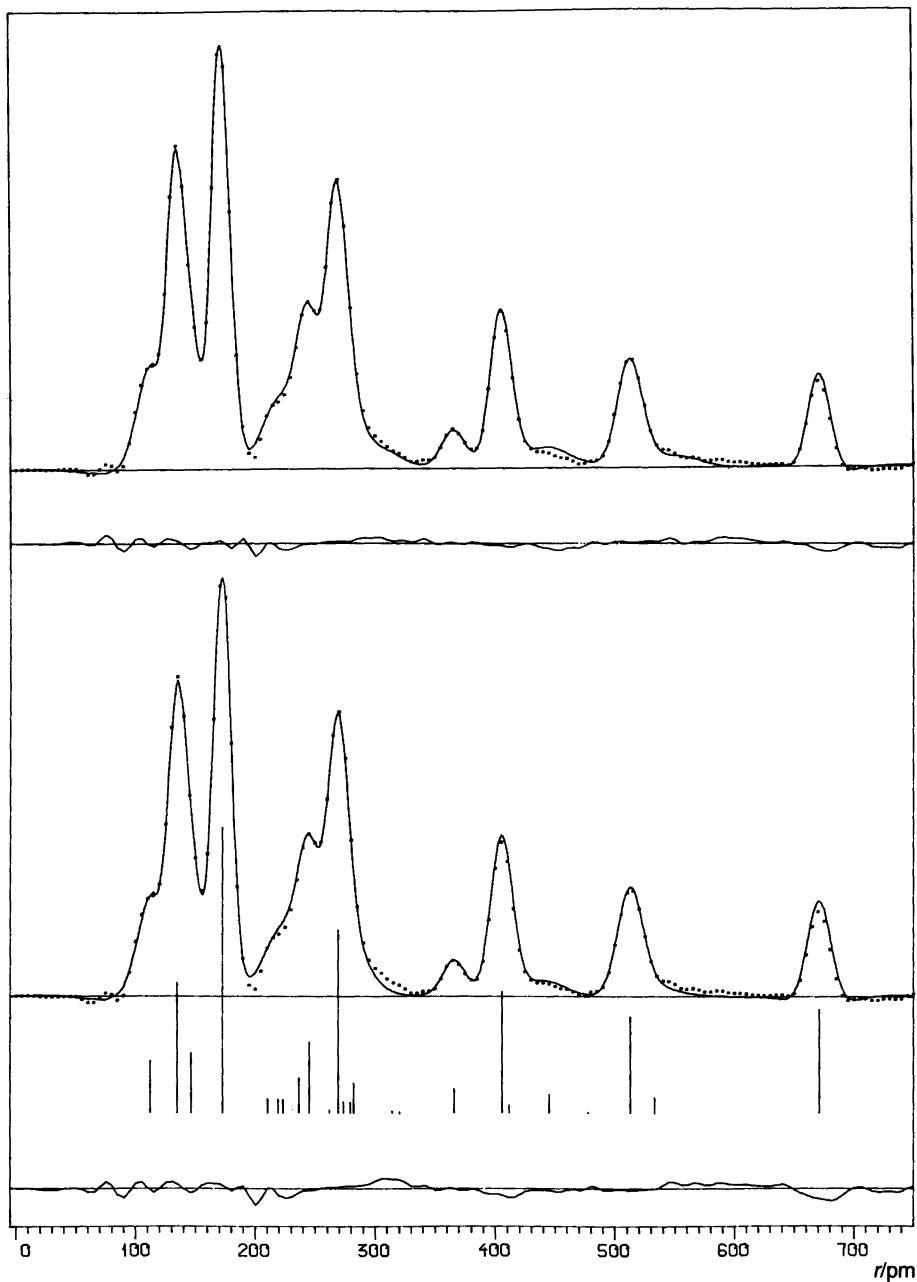


Fig. 4. Experimental RD curves for (●) *trans,trans*-1,4-dichloro-1,3-butadiene (TT2) calculated from the 310 K data (cf. Table 1) using damping coefficient of  $1.5 \cdot 10^{-5} \text{ nm}^2$ . They are compared to theoretical counterparts (—) and differences are given. They correspond to 100% of *anti* TT2 (lower) and to the final results (upper) obtained with vapour composition as explained in the text (cf. Table 2). The distance distributions (cf. Table 3) are indicated by vertical bars (see also Fig. 8).



Table 5. Least-squares standard deviations ( $\sigma_{LS}$ ) and correlation matrix ( $100e_{ij}$ ) for TT2.

Parameter	$\sigma_{LS}^a$	$100e_{ij}$
r(C-H)	0.4	100
r(C=C)	0.10	45 100
r(C-C)	0.2	19 41 100
r(C-Cl)	0.06	-2 -2 9 100
$\angle(C=C-C)$	0.3	-27 -50 -79 -15 100
$\angle(C3-C2-H)$	1.1	2 4 8 -1 13 100
$\angle(C2=C1-H)$	1.2	-26 -18 -24 -7 61 42 100
$\angle(O=C-Cl)$	0.13	-5 -37 -15 -25 -16 -43 -60 100
r <sub>1</sub>	0.4	8 26 20 8 -20 2 -8 -12 100
r <sub>3</sub>	0.18	-27 -1 -22 11 12 -11 5 -1 17 100
r <sub>5</sub>	0.10	-29 -20 -1 -3 0 -16 2 14 -4 17 100
r <sub>6</sub>	0.3	17 16 15 3 -44 -37 -60 47 2 0 -1 100
r <sub>7</sub>	0.14	-25 -12 0 -7 0 20 14 3 -3 13 30 7 100
r <sub>8</sub>	0.18	-10 -2 3 1 -2 1 1 0 0 11 19 -3 9 100
r <sub>11</sub>	0.8	-12 -3 -14 -10 16 -32 17 3 -4 8 -3 24 0 -2 100
r <sub>16</sub>	0.8	-5 -3 -1 -5 6 -2 10 -3 -2 0 3 0 3 -19 8 100
r <sub>17</sub>	0.3	-3 1 6 0 -10 -10 -13 11 2 7 14 8 6 7 -2 0 100
r <sub>20</sub>	0.2	-6 0 -1 -1 3 0 5 -2 1 5 9 -4 5 13 1 -1 12 100
$\alpha_1$	2	7 5 -10 -3 16 16 13 -14 2 -8 -22 -13 -10 9 0 -5 8 27 100
$\alpha(CT2)$	1.8	-7 -1 0 0 -2 -14 -4 5 0 5 10 3 0 9 2 -1 3 3 -61 100
S(1)	2	-21 -9 3 0 -6 -20 -1 9 -3 17 35 4 17 15 4 2 8 4 -69 90 100
S(2)	3	-21 -6 6 -2 -8 -19 -3 10 1 25 50 8 25 22 5 1 13 9 -59 78 86 100

<sup>a</sup>Distances and amplitudes in pm, angles in degrees; S are scale factors for the two data sets: S(1) = 109 and S(2) = 105. Mole fractions  $\alpha$  in %.

this feature is the suspicion that at 310 K the gas does not contain 100% of *anti* TT2, but rather some 85%. However, further interpretations of the RD curve do not suggest large contributions from *syn* forms (cf. Fig. 8) although we could not exclude the presence of about 5% of a *synclinal* form for which a  $\varphi_2$  value of about  $55^\circ$  appeared to be preferred. A CT2 contamination as indicated by the vibrational spectra (cf. Experimental) was also considered and ultimately, the struc-

tural and vibrational parameters for *anti* TT2 were refined together with the composition of the gas, assuming the coexistence of both a second form ( $\varphi_2 = 55^\circ$ ) and CT2. This best refinement [ $R(\text{tot}) = 7.49\%$ ] gave  $\alpha_2 = 4(4)\%$  and  $\alpha(\text{CT2}) = 11(3)\%$ , and the results for *anti* TT2 are presented in Tables 2, 3 and 5. The corresponding difference intensities and RD curves are included in Figs. 2 and 4, respectively.

The short-camera plates of the 283 K and 473

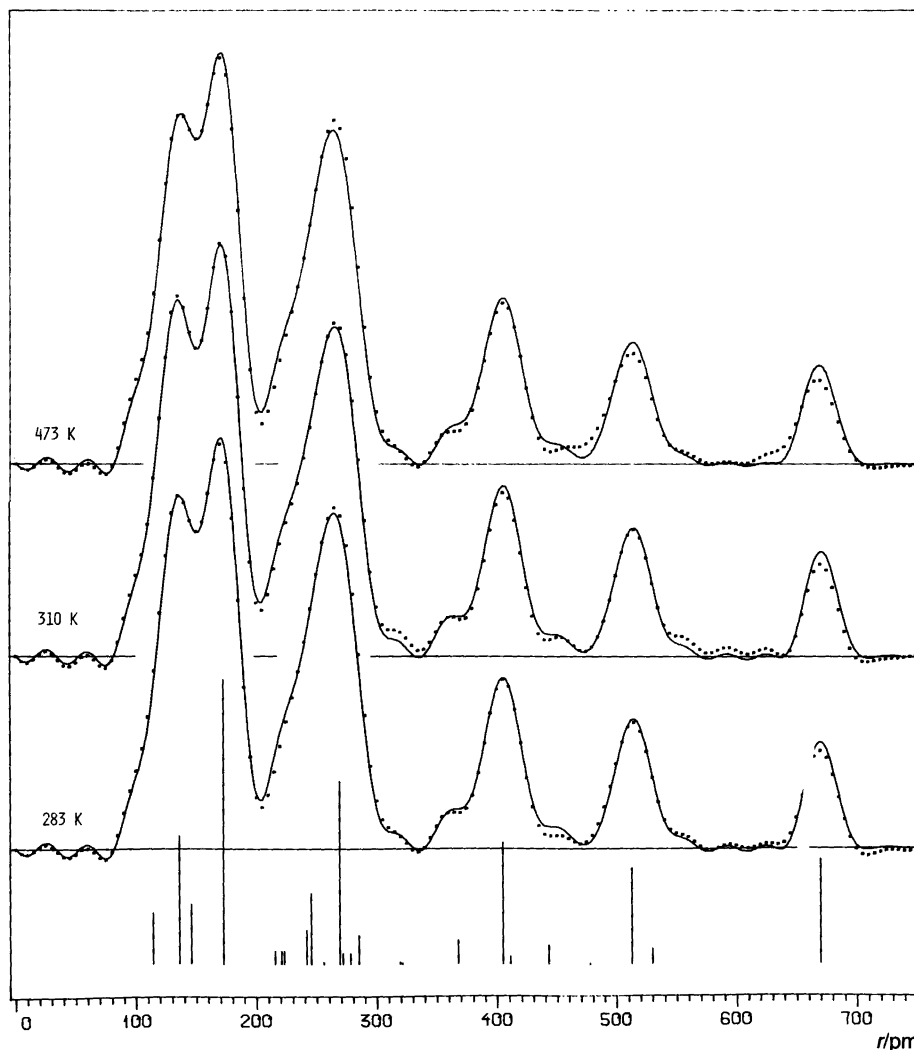


Fig. 5. Experimental RD curves (●) for *trans,trans*-1,4-dichloro-1,3-butadiene (TT2) calculated from the 48 cm camera data (cf. Table 1) at three temperatures compared with theoretical counterparts corresponding to 100% of the *anti* conformer. The damping coefficient is  $6.0 \cdot 10^{-5} \text{ nm}^2$ . The distance distribution (cf. Table 3) is indicated by vertical bars (see also Fig. 8).

K experiments were of poor quality and we have chosen to present the temperature effect on the RD curve of TT2 in the form of the 48 cm data for all three temperatures. These experimental RD curves are compared in Fig. 5 with theoretical counterparts assuming 100% presence of the *anti* form and using calculated values for all vibrational parameters. The 283 and 473 K data sets were both recorded using a second sample of TT2 (cf. Experimental) and analyses of these GED

data indicated less than 5% of CT2. Differences between the RD curves for these two temperatures point to differences in the gas composition. In contrast, in both low temperature RD curves the RD curve for 473 K clearly showed contributions at 630 to 650 pm and 460 to 480 pm which may be assigned to Cl...Cl and C...Cl interactions of a *syn* form (cf. Fig. 8). This is matched with area deficiencies at 670 and 515 pm which correspond to the lengths of these interac-

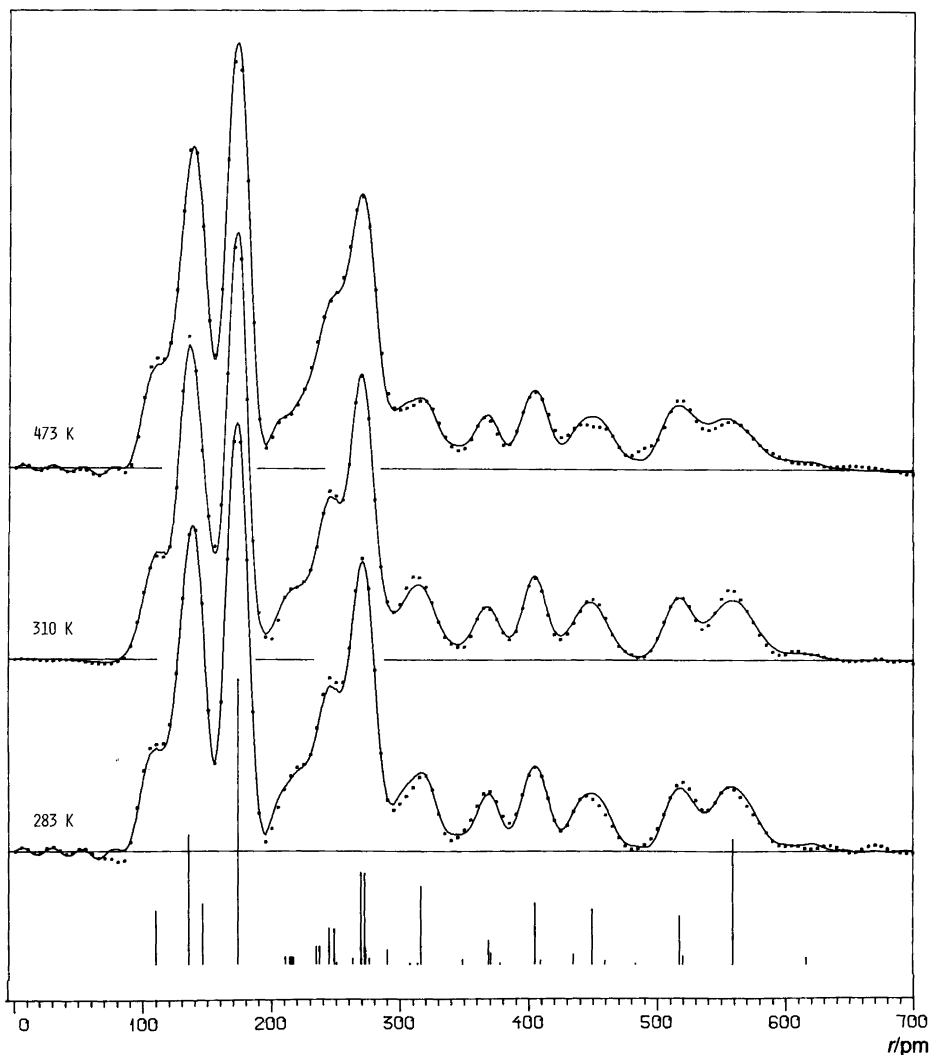


Fig. 6. Experimental RD curves for (●) *cis,trans*-1,4-dichloro-1,3-butadiene (CT2) at three temperatures using varying data ranges as specified in Table 1 and damping coefficient of  $1.5 \cdot 10^{-5} \text{ nm}^2$ . They are compared to theoretical counterparts (—) corresponding to 100% of the *anti* conformer. The distance distributions (cf. Table 4) are indicated by vertical bars (see also Fig. 8).

Table 6. Least-squares standard deviations ( $\sigma_{LS}$ ) and correlation matrix ( $100\sigma_{ij}$ ) for CT2.

Parameter	$\sigma_{LS}^a$	$100\sigma_{ij}$
r(C-H)	0.3	100
r(C-C)	0.18	17 100
r(C=C)	0.07	37 29 100
r(C-Cl)	0.04	-5 11 -2 100
$\angle(C=C-C)$	0.2	-19 -61 -26 -4 100
$\Delta(C=C-C)$	0.3	-6 -1 -21 -16 -28 100
$\angle(C-C-H)$	1.2	12 4 11 -17 4 -13 100
$\angle(C=C-H)$	0.6	-17 -13 -12 -5 37 -8 22 100
$\angle(C=C-Cl)$	0.17	5 31 -4 -4 -71 49 -20 -23 100
$\Delta(C=C-Cl)$	0.3	-10 -41 -19 -9 62 -29 6 2 -85 100
$\tau_1$	0.3	11 21 32 8 -16 -10 0 -8 2 -11 100
$\tau_5$	0.14	-35 -40 -1 10 22 0 -8 5 -16 16 2 100
$\tau_8$	0.08	-28 -3 -20 -1 -3 1 -18 4 5 3 -7 22 100
$\tau_{10}$	0.3	17 6 8 7 -40 28 -21 -68 32 -11 3 -1 0 100
$\tau_{12}$	0.11	-29 -19 -20 -11 17 -5 6 12 -22 32 -11 24 35 4 100
$\tau_{14}$	0.3	-4 7 0 8 -8 -3 -13 -6 5 -4 2 10 18 0 -2 100
$\tau_{15}$	0.2	-7 3 -2 0 -7 -7 17 -1 2 -2 0 9 15 0 -4 100
$\tau_{16}$	0.9	25 7 10 1 -36 -19 40 -16 12 -4 2 -7 -4 19 -4 0 13 100
$\tau_{18}$	0.4	-3 0 -4 -2 4 6 -11 3 -2 5 -2 0 5 1 4 2 -17 -12 100
$\tau_{32}$	0.3	-4 2 -1 -1 8 -14 -2 0 -8 11 0 4 11 0 11 1 1 0 3 100
$\tau_{33}$	0.3	-7 4 -5 1 -15 8 -2 -3 17 -16 -1 5 12 5 3 5 6 3 0 -8 100
$\tau_{37}$	0.3	0 -1 0 -2 0 6 1 2 0 -2 0 0 0 0 0 -1 0 -2 1 -1 -14 100
S(1)	0.4	-38 5 -19 2 -4 -4 -10 15 5 0 -7 35 65 -6 42 19 21 -5 8 12 15 0 100
S(2)	0.7	-25 8 -8 -1 -9 -1 -6 0 4 0 1 34 68 6 42 20 21 -1 5 12 13 0 57 100

<sup>a</sup>Distances and amplitudes in pm, angles in degrees; S are the scale factors for the two data sets: S(1) = 50.1 and S(2) = 49.3.

tions in the *anti* form. Thus, significant amounts of a minor form appear to be present at this temperature, and the best refinement gave 15 (3)% of a *synclinal* form with  $\varphi_2 = 52(14)^\circ$ . It should be noted that the lengths of the mentioned  $\text{Cl}\cdots\text{Cl}$  and  $\text{C}\cdots\text{Cl}$  interactions are rather insensitive to torsion angle changes in the  $0$  to  $60^\circ$  range (cf. Fig. 8). This accounts for the large uncertainty associated with the obtained  $\varphi_2$  value, but more importantly, the assumption of rigid torsion must be considered in context with this situation. Even small differences in, for example,  $\angle(\text{C}=\text{C}-\text{C})$  for the two forms could affect the  $\varphi_2$  determination significantly, and it appears that planar *syn* ( $\varphi_2 = 0^\circ$ ) cannot be entirely ruled out.

*Refinements and results for CT2.* Fig. 6 shows the agreement between experimental and theoretical RD curves in the 100% *anti* interpretation of the data for the three experimental temperatures us-

ing values for the amplitude parameters as calculated for appropriate temperatures. It should be noted that the 273 K and 473 K intensities had rather high noise-to-signal ratios as well as limited data ranges (cf. Tables 1). The 310 K data could be satisfactorily interpreted in terms of 100% of the planar *anti* form. Results of a final refinement which includes several independent  $l$  values and  $l$  value groups are presented in Tables 2, 4 and 6. The goodness of fit is demonstrated by the least-squares  $R$  factors (Table 2), and the difference intensities and difference RD curves shown in Figs. 3 and 7, respectively. It was not possible to resolve corresponding bond distances in the *cis* and *trans* moieties of the molecule, and ultimately the assumptions specified in Table 2 were used. However, it is remarkable that the principal contributions to the RD curve beyond 300 pm for this unsymmetric molecule are contained in well resolved peaks. Consequently, it

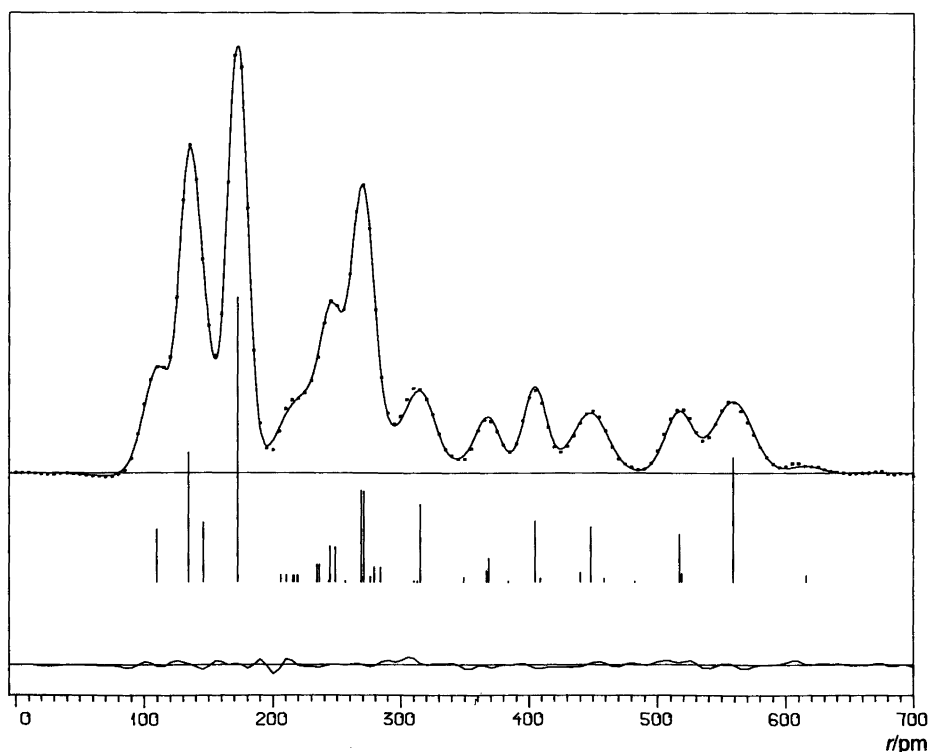


Fig. 7. Experimental RD curve (●) calculated from the 310 K intensities (cf. Table 1), the final theoretical counterparts (—) and the corresponding difference RD curves (below) for *cis,trans*-1,4-dichloro-1,3-butadiene (CT2). The damping coefficient is  $1.5 \cdot 10^{-5} \text{ nm}^2$ . The distance distribution (cf. Table 4) is indicated by vertical bars (see also Fig. 8).

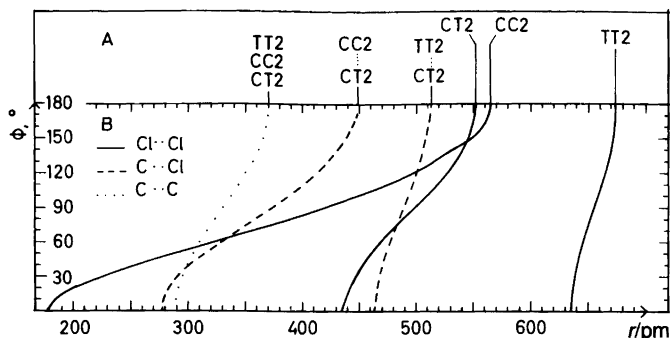


Fig. 8. The lengths of important torsion-sensitive interatomic interactions as a function of the torsional angle  $\varphi$  in the *cis,cis*, *trans,trans* and *cis,trans* isomers of 1,4-dichloro-1,3-butadiene, CC2, CT2 and TT2, respectively.

was possible to refine difference parameters for the C=C-C and C=C-Cl angles so as to give  $p(\text{trans}) = p(\text{cis}) + \Delta p$  (cf. Table 2).

Refinements that included the two-conformer possibility indicated that small contributions from a *synclinal* form with preferred  $\varphi_2$  values of 40 to 50° could not be ruled out at 310 K. Fig. 8 shows that in this case small parts of the contributions are shifted from the 560 pm (Cl...Cl), 520 pm (C...Cl) and 450 pm (C...C) regions to already established peaks at 450, 470 and 310 pm, respectively. Comparisons of the RD curves of Fig. 6 show that the composition of the gas at 473 K is different from that at the two lower temperatures, but the second component must rather contribute to the RD curve at about 490 pm. A two-conformer refinement gave  $\alpha_2 = 5(2)\%$  and  $\varphi_2 = 85(8)^\circ$ , and only a small improvement in the least-squares agreement factor.

## Discussion

The results of our conformational analyses are rather inconclusive, and more so for CT2 than for TT2. The notion based on 310 K data that the vapour of CT2 might contain 5% of a *syn* form with a  $\varphi$  value of 40–50° appears reasonable, but it is incompatible with the lower quality 473 K data which failed to reveal any increased contribution from this form at elevated temperature, rather preferring 5% of an unexpected, nearly perpendicular form. For TT2, however, the same second form was indicated in reasonable amounts (5 to 15%) by analyses of the 310 and 473 K data. However, it has been pointed out that the determination of its conformational angle ( $\varphi_2 = 52$

(14)°) is ambiguous, and that the planar *syn* form cannot be ruled out entirely. Thus, reliable characterization of the minor conformer of TT2 is crucially dependent on reasonable model assumptions. This requires higher proportions of the minor form (i.e. higher experimental temperatures) so that important valence angles can be refined independently for the two conformers, and preferably also supporting information about conformational structure variations from reliable computational methods.

The structure parameters obtained for the *anti* forms appeared to be insensitive to various assumptions considered regarding the gas composition, such as the presence of minor forms or contaminants, and analyses of the various data sets gave consistent results. The final structural parameters given in Table 2 are those obtained from the 310 K data for reasons explained in the experimental section, and the corresponding results of the analogous study of CC2 are included. Further structural comparisons with related compounds are given in Table 7.

It is seen that the structures of the C=CHCl moieties of the 1,4-dichloro compounds (CC2, TT2 and CT2) are similar to that of vinyl chloride (MCl, Table 7), but that there is a slight widening of the C=C-Cl(*cis*) angles as compared to  $\angle(\text{C}=\text{C}-\text{Cl})$  in the *trans* moieties and in vinyl chloride. This may be related to repulsions between substituents in the *cis*-1(4) and 3(2) positions of the carbon skeleton, i.e. Cl...H interactions (cf. Fig. 1). The wider C=C-C angles observed in CC2 and the *cis* moiety of CT2 as compared with the C=C-C angles in TT2, in the *trans* moiety of CT2 and in butadiene (BUT,

Table 7. Comparison of structural parameters for *anti* forms of 1,3-butadiene (BUT), and its 2,3-dichloro (D23), *cis,cis*-1,4-dichloro (CC2), *trans,trans*-1,4-dichloro (TT2) *cis,trans*-1,4-dichloro (CT2), 2-chloro (M2), *cis*-1-chloro (MC1) and *trans*-1-chloro (MT1) derivatives; and for ethene (ETH) and its monochloro (MC1) derivative.

	C2-C3	C1=C2 C=C4	C1-Cl C4-Cl	C2-Cl C3-Cl	C1=C2-C3 C4=C3-C2	C2=C1-Cl C3=C4-Cl	C3-C2-Cl C2-C3-Cl	Ref.
BUT( $r_a$ )	146.7(3)	134.4(3)	—	—	122.8(5)	—	—	3b
BUT( $r_g$ )	146.3(3)	134.1(2)	—	—	123.3(5)	—	—	3c
D23( $r_a$ )	147.2(4)	133.7(2)	—	174.5(2)	126.1(2)	—	115.2(3)	5
M2( $r_s$ )	144.7(9)	134.9(5)	—	174.1(9)	123.9(6)	—	119.7(7)	8
		134.1(4)	—	—	125.8(3)	—	—	
CC2( $r_a$ )	145.6(5)	134.3(3)	173.1(3)	—	125.1(3)	123.7(2)	—	4
MC1( $r_s$ )	144.9(13)	132.7(6)	173.1(8)	—	126.5(3)	123.7(3)	—	6
		134.3(2)	—	—	123.0(7)	—	—	
TT2( $r_a$ )	146.2(5)	134.1(2)	172.4(2)	—	121.9(6)	122.7(3)	—	This work
MT1( $r_s$ )	143.9(6)	131.3(10)	173.7(4)	—	124.1(11)	123.5(7)	—	7
		134.0(7)	—	—	124.8(10)	—	—	
CT2( $r_a$ ) <i>c</i> :	145.6(4)	134.1(2)	172.3(2)	—	125.6(4)	123.9(3)	—	This work
<i>t</i> :		134.1(2)	172.3(2)	—	122.0(6)	122.9(4)	—	
ETH( $r_g$ )	—	133.7(2)	—	—	—	—	—	15
MCl( $r_g$ )	—	134.2(4)	173.0(4)	—	—	122.5(2)	—	16

<sup>a</sup>Distances in pm and angles in degrees;  $r_s$  structures by MW, others by GED ( $r_g = r_a + I^2/r$ ).

Table 7) also suggest H...Cl repulsions in the H-C-C=C-Cl (*cis*) fragment of the molecules. D23 and M2 have Cl-C-C=C-H (*cis*) arrangements which also exhibit wide C=C-C angles.<sup>15,16</sup>

It appears that terminal C-Cl bonds are rather similar in length to the C-Cl bonds in vinyl chloride, but slightly shorter than the central C-Cl bonds encountered in D23 and M2. Comparisons of  $r(\text{C}=\text{C})$  for the distributed butadienes (D23, CC2, TT2 and CT2) and for the parent molecule (BUT), as well as of  $r(\text{C}=\text{C})$  in vinyl chloride and ethene, suggest that chlorine substitution does not affect the length of the C=C bond significantly in these compounds. The  $r_s$  structure of M2 is also consistent with this notion, whereas the  $r_s$  structures of MC1 and MT1 suggest short C=C bonds in the substituted moiety of the molecules. This has been discussed in terms of Cl...H interactions,<sup>6,7</sup> but it is remarkable that similar effects are not observed for the distributed molecules. Also, the central C-C bonds of all the three monochlorobutadienes appear short as compared to the results for the other compounds. However, the  $r_s$  structures have no well-defined relation to other types of structural parameters. The differences between  $r_g$  and  $r_s$  parameters are estimated to be  $1 \pm 1$  pm, but it is noted that they sometimes deviate from

this range with no apparent systematic trend.<sup>17</sup> It has also been stressed that caution should be exercised in comparisons between  $r_s$  parameters for related compounds, and consequently with other types of structural parameters, for molecules with relevant atoms close to a principal axis. To provide a basis for more meaningful structural comparisons it seems worthwhile to determine the structures of M2, MC1 and MT1 by joint analyses of GED intensities and the literature<sup>6-8</sup> microwave rotational constants. Such studies, including also results from MO calculations, are in progress.<sup>18</sup>

**Acknowledgements.** We are grateful to cand. real. Arne Almenningen and siv. ing. Ragnhild Seip for recording the electron diffraction diagrams, to Mrs. Snefrid Gundersen and Mr. Hans V. Volden for carrying out the densitometric measurements on the photographic plates, and to Dr. Fred Karlsson, University of Stockholm, for supplying samples for these investigations. Financial support from the Swedish Natural Science Research Council to Z. S. is gratefully acknowledged. In particular we wish to express our gratitude to Professor Otto Bastiansen for many stimulating discussions and for support throughout the years.

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Received November 2, 1987.