

Structure of Gaseous and Crystalline 2,2'-Dichlorobiphenyl

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The structure of 2,2'-dichlorobiphenyl has been examined in the gaseous phase by the electron-diffraction technique and in the crystalline state by X-ray diffraction. The twist angle about the central carbon-carbon bond is approximately 70° and only slightly larger in the gas phase than that in the solid in contrast to what has been found for biphenyl. Only one stable conformer was detected in the gas phase at 300 °C.

Bastiansen and coworkers studied biphenyl^{1,2} and a series of ortho-substituted biphenyls (2,2'-difluoro-,³ 2,2'-dichloro-,⁴ 2,2'-dibromo-,⁴ and 2,2'-diiodo-biphenyl⁴) by electron-diffraction methods several years ago. More recently other related compounds, including perfluorobiphenyl,⁵ have also been studied. (See Ref. 6 for a more detailed discussion). The angle between the ring planes (ϕ) in biphenyl was found to be about 42° in the gaseous phase whereas the molecule is planar ($\phi=0$) in the crystal.⁷⁻⁹ The angle ϕ found in some of the biphenyls is given in Table 1.

Semi-empirical calculations¹⁰⁻¹² of the variation in the conjugation and van der Waals

Table 1. Angle of twist in biphenyl and some substituted biphenyls. $\phi=0$ corresponds to the *syn* form.

Compound	ϕ (obs), gas phase	ϕ (calc)
Biphenyl	42, ³ 0 (solid) ⁷	40 ¹¹
2,2'-Difluorobiphenyl	60 ³	42, 143 ⁵
2,2'-Dichlorobiphenyl	74 ⁴	72, 120 ⁵
2,2'-Dibromobiphenyl	75 ⁴	82, 112 ⁵
2,2'-Diiodobiphenyl	79 ⁴	93 ⁵
Perfluorobiphenyl	70 ⁵	46 ⁵

energies as a function of ϕ lead to a flat minimum at about 40° from planarity in biphenyl in good agreement with the electron diffraction result. The barrier heights obtained were 2–4 kcal/mol, the barrier at $\phi=0^\circ$ probably being slightly higher than that at $\phi=90^\circ$.

The CNDO/2 method has also been applied to biphenyl^{13,14} and perfluorobiphenyl.¹⁴ The calculations in both cases gave an energy minimum for ϕ close to 90° in contrast to the experimental values.

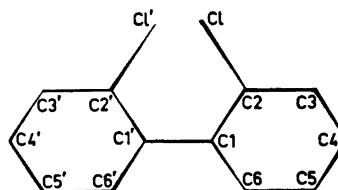


Fig. 1. 2,2'-Dichlorobiphenyl.

The most stable conformers of the 2,2'-dihalo-biphenyls are closer to the *syn* ($\phi=0^\circ$) than to the *anti* ($\phi=180^\circ$) form. Extension of the semi-empirical calculations which gave promising results for biphenyl, to these compounds,^{5,15} yielded two energy minima for the fluoro-, chloro-, and bromocompounds. In contradiction to the experimental results the calculations gave a lower minimum for $\phi > 90^\circ$ than for $\phi < 90^\circ$.

The results of the calculations led us to reinvestigate 2,2'-dichlorobiphenyl by electron diffraction to see if there was evidence for a second conformer with $\phi > 90^\circ$. In order to increase the amount of a possible less stable conformer, the nozzle temperature was as high as 300 °C, though a lower temperature would be

preferable for an accurate determination of the molecular parameters, especially the twist angle ϕ . At the same time we have determined the structure in the solid by X-ray diffraction methods in order to observe any change in the conformation as well as to compare the molecular parameters obtained by the two methods. In the earlier work on the conformation of 2,2'-dihalobiphenyls in the gas phase two assumptions have been made: that each of the chlorophenyl parts are planar and that the C4-C1-C1'-C4' arrangement is linear. Deviations from these conditions make at least three definitions of ϕ possible; ϕ may be defined as the angle formed by the best plane through all the atoms of each of the chlorophenyl parts, as the angle between the best planes through the carbon atoms of each ring or it may be defined as the dihedral angle C2C1C1'C2'. In a deformed molecule the three angles are not equal and this must be taken into account when the results from the two methods are discussed.

CRYSTAL STRUCTURE DETERMINATION

Experimental

The sample of 2,2'-dichlorobiphenyl was obtained from Monsanto Chemical Co. Single crystals were formed by slow diffusion of water into a solution of the compound in ethanol. The crystals sublime and had to be kept in a capillary tube during the X-ray experiments. The specimen used was approximately shaped as a cube with edges of about 0.3 mm.

Oscillation, Weissenberg and precession films indicated orthorhombic symmetry. Conditions for the presence of reflections were $h+k$, $k+l$ and $h+l$ even for hkl , $k+l=4n$ for $0kl$, and $l+h=4n$ for $h0l$. This characterizes the space group uniquely to be $Fdd2$.

Unit cell dimensions were determined from diffractometer measurements. A manual Picker four-circle diffractometer with $\text{CuK}\beta$ radiation ($\lambda=1.3922 \text{ \AA}$) was used. The computer program applied for the least-squares calculations as well as other programs applied during the X-ray structure analysis are described in Ref. 16.

Three-dimensional intensity data were recorded on an automatic Picker four-circle diffractometer using graphite crystal monochromated $\text{MoK}\alpha$ radiation. The $\theta-2\theta$ scanning mode with a 2θ scan speed of 1° min^{-1} was applied through the scan range of 0.7° below $2\theta(\alpha_1)$ to 0.8° above $2\theta(\alpha_2)$. Background counts were taken for 25 sec at each of the scan range limits. The take-off angle was 4° and the temperature was kept constant at 18

$^\circ\text{C}$. The intensities of three standard reflections were measured for every 100 reflections of the data set. They showed a variation of up to 5.5% and the data were accordingly adjusted. The standard deviations in the intensities were taken as the square root of the total counts with the addition of 2% of the net intensity.

The measurements included 799 reflections with $\sin \theta/\lambda$ less than 0.6 \AA^{-1} ; of these 734 had intensities larger than twice their standard deviations and were regarded as observed. The remaining reflections were excluded from the refinement procedure.

Atomic form factors used were those of Hansen *et al.*¹⁷ for chlorine and carbon, and of Stewart *et al.*¹⁸ for hydrogen.

Crystal data

2,2'-Dichlorobiphenyl, $\text{C}_{12}\text{H}_8\text{Cl}_2$, orthorhombic. $a=23.913(0.006) \text{ \AA}$; $b=13.469(0.007) \text{ \AA}$; $c=6.637(0.004) \text{ \AA}$.

$V=2137.7 \text{ \AA}^3$; $M=223.10$; $F(000)=912$; $\mu=0.056 \text{ mm}^{-1}$; $Z=8$.

$D_{\text{obs}}=1.33 \text{ g cm}^{-3}$, $D_{\text{calc}}=1.386 \text{ g cm}^{-3}$.

Absent reflections: $hkl:h+k$ and $k+l$ odd, $0kl$ other than $k+l=4n$, $h0l$ other than $h+l=4n$. Space group $Fdd2$.

Structure determination and refinement

The space group symmetry requires the molecule to possess a two-fold axis of symmetry. The positions of the chlorine atom and the six carbon atoms were readily derived from a sharpened Patterson synthesis. After a preliminary refinement of the coordinates the positions of the four hydrogen atoms were calculated from stereochemical considerations. All positional parameters (except for one origin-fixing z -coordinate), anisotropic thermal parameters for the heavy atoms and isotropic thermal parameters for hydrogen atoms were refined by least-squares calculations minimizing the function $\sum w(F_o - F_c)^2$. The weight w assigned to each reflection was the inverse of the variance of the structure factor. The refinement converged with a final conventional R factor of 0.035, $R_w=0.043$. A difference Fourier map showed no electron density larger than 0.35 e \AA^{-3} .

The experimental data may be obtained at request from the authors. Final parameters are listed in Table 2 and interatomic distances and

Table 2. Fractional (crystallographic) atomic coordinates and thermal parameters with estimated standard deviations ($\times 10^5$ for Cl and C; $\times 10^4$ for H). The temperature factor is $\exp -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁ (<i>B</i>)	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
Cl	7081	-1705	66243	213	740	2389	-14	-404	634
	3	5		1	5	17	4	8	16
C1	1666	4669	32647	133	493	1794	13	60	29
	10	17	41	4	12	55	11	25	46
C2	5702	6794	47117	144	503	1940	36	-36	117
	10	17	42	4	12	56	12	25	46
C3	8896	15290	46498	164	590	2977	-68	-125	-212
	12	20	54	5	15	86	14	34	61
C4	8087	22026	30983	199	594	3564	157	299	239
	13	24	64	5	17	101	15	41	70
C5	4115	20224	16549	236	694	2923	59	119	878
	14	23	64	6	16	86	17	41	73
C6	1024	11637	17378	195	635	2084	47	132	447
	12	22	53	6	16	62	14	34	58
HC3	1174	1636	5677	5.2					
	14	23	65	0.7					
HC4	1005	2799	2912	3.8					
	12	20	56	0.6					
HC5	347	2747	682	5.9					
	14	19	70	0.8					
HC6	-85	953	763	6.8					
	16	28	78	1.0					

Table 3. Interatomic distances (Å) and bond angles (°) found by X-ray diffraction. Estimated standard deviations (in parentheses) apply to the least significant figure.

Distance	Corrected	Angle	
Cl-C2	1.741(3)	Cl-C2-Cl	120.0(2)
Cl-C2	1.392(4)	C3-C2-Cl	117.6(2)
C2-C3	1.376(4)	Cl-C2-C3	122.4(2)
C3-C4	1.386(5)	C2-C3-C4	119.3(3)
C4-C5	1.371(6)	C3-C4-C5	120.0(3)
C5-C6	1.374(4)	C4-C5-C6	119.6(8)
C1-C6	1.390(4)	C1-C6-C5	122.6(3)
C1-C1'	1.489(5)	C2-C1-C6	116.2(2)
Cl-Cl'	3.418(2)	Cl'-C1-C6	120.8(2)
C-H	0.98 (mean value)	Cl'-C1-C2	123.0(2)

bond angles are given in Table 3. The r.m.s. deviation of the experimental U_{ij} values from those calculated from a rigid-body analysis of the molecule was 0.0025 \AA^2 . The r.m.s. amplitudes of translation along the principal axes are 0.22, 0.19, and 0.18 \AA and the librations have r.m.s. amplitudes of 5.3° , 3.4° , and 2.6° about the principal axes, the largest amplitude

being about the axis of the least moment of inertia. Corrections in bond lengths were derived from the rigid-body librations.

Interatomic distances and bond angles are listed in Table 3. Standard deviations were derived from the correlation matrix ignoring standard deviations in cell parameters.

The values obtained for the bond lengths

are discussed in the last section. However, some comments on the bond angles are given here since they were used as input parameters in the gas phase investigation. The internal angles of the phenyl rings deviate significantly from

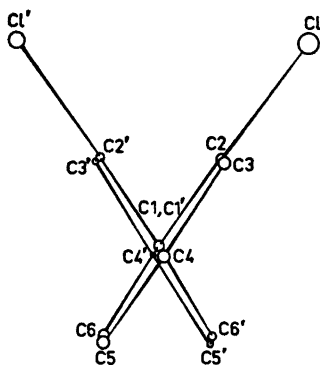


Fig. 2. 2,2'-Dichlorobiphenyl as seen along the central carbon-carbon bond.

120°. This is also found for biphenyl itself in which the C2C1C6 angle was found to be 116.8° (117.4 corrected for thermal vibration effects).⁸ The decrease in the corresponding angle in the present structure is 4° from the benzene value, an increase of about 2.5° is found in the internal angles at C2 and C6.

The external angles at C1 and C2 are deformed, probably to relieve the strain caused by the fairly short intramolecular Cl-Cl distance (3.42 Å). The C1'C1C2 angle is thus by 2° larger than C1'C1C6 and C1C2C1 by 2.5° larger than C1C2C3. Furthermore, the C-Cl bond is bent out of the plane of the benzene ring by 2.3° and the Cl-Cl bond forms an angle of 1.9° with this plane. The deformation of the molecule may be seen from Fig. 2 which shows the molecule as seen along the central C-C bond. The carbon atoms of each phenyl ring is strictly coplanar, the largest deviation from a least-squares plane being 0.007 Å

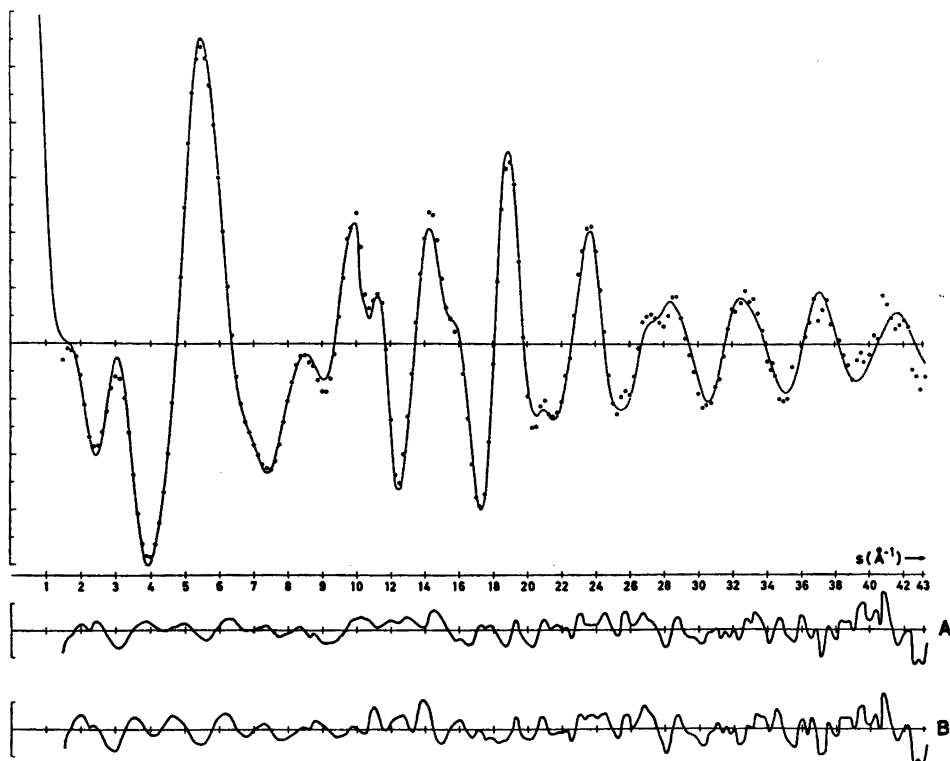


Fig. 3. Experimental (dotted) and theoretical intensity functions for 2,2'-dichlorobiphenyl. The theoretical curve corresponds to model A. The lower part of the curve shows the differences between experimental and theoretical values for model A and model B.

Including the chlorine atom in the least-squares plane the deviations vary between 0.01 and 0.03 Å.

The "twist angle" about the C1-C1' bond may now be calculated to be as follows (*cf.* the introductory remarks): The angle between the least-squares planes through the chlorophenyl moieties is 68.5°; the angle between the corresponding planes excluding the chlorine atoms is 66.8°; the dihedral angle C2'C1'C1C2 is 69.2°.

ELECTRON DIFFRACTION INVESTIGATION

Experimental

Two sets of diffraction diagrams were recorded by the Oslo unit,¹⁹ with nozzle-to-plate distances of 480.12 mm (set I) and 200.81 mm (set II), respectively. The nozzle temperature was about 300 °C and the electron wave-length 0.06458 Å. The data from five

plates from set I (s range 1.50 Å⁻¹ to 19.125 Å⁻¹) and four plates from the II (s range 7.25 Å⁻¹ to 44.0 Å⁻¹) were plotted and found satisfactory. A composite intensity curve was then calculated (see Fig. 3).

The data were processed in the usual way.²⁰ The modified molecular intensities were calculated using the modification function

$$s/(|f_c'| + |f_{Cl}'|).$$

The elastic scattering amplitudes were calculated for the applied accelerating potentials by the partial wave method.²¹ The atomic potentials for carbon and chlorine were from Ref. 22, for hydrogen from Ref. 18.

Structure determination and refinement

An experimental radial distribution (RD) curve²⁰ (see Fig. 4) was calculated by Fourier transformation of the experimental intensity

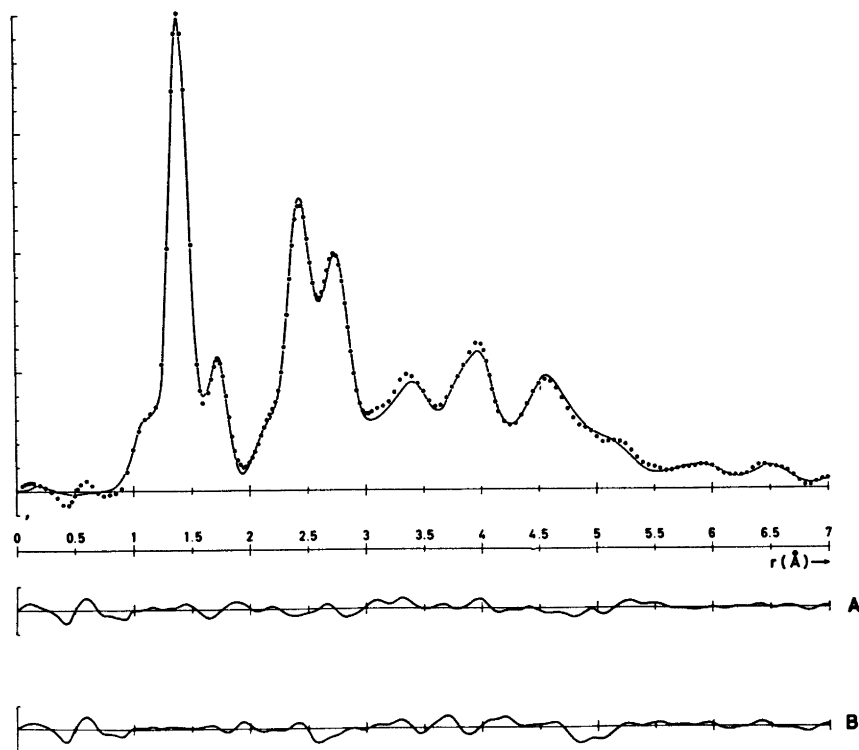


Fig. 4. Experimental (dotted) and theoretical radial distribution functions for 2,2'-dichlorobiphenyl (artificial damping, $k = 0.002$ Å²) calculated by Fourier inversion of the curves in Fig. 3. Difference curves corresponding to those in Fig. 3 are also shown.

curve in Fig. 3. Comparison with theoretical RD curves showed, in agreement with the previous investigation, that the main conformer is closer to *syn* than to *anti*, and that the amount of a possible second conformer must be small. The structure was therefore refined by the least-squares method, assuming one conformer only.

Two models were considered in the calculations. The independent parameters which may be refined, were the same in both models, *i.e.*

(C-C) _{ring}	(all assumed equal)
C-C1'	
C-Cl	
C-H	(all assumed equal)
∠C1C2C1	
∠C1C6H6	

β : angle between the CCl bond and the ring plane

ϕ : angle of twist about the bridge bond

The models differ in the assumptions about the bond angles.

Model A: All bond angles except those involving Cl and H6 were assumed to be 120°.

Model B: The X-ray results show that the angles in the ring deviate somewhat from 120°. The following values, which are close to the X-ray results, were therefore tried in the electron-diffraction study.

∠C2C1C6 = 116.2°
∠C1C2C3 = C1C6C5 = 122.9°
∠C2C3C4 = C6C5C4 = 119.0°
∠C3C4C5 = 120°.

It was not possible to refine the angles β and ϕ simultaneously. Refinements were therefore carried out with fixed values of β . With $\beta = 0^\circ$ ϕ was found to be 75.0° for model A and 72.2° for model B. With $\beta = 2^\circ$, *i.e.* close to the result obtained in the X-ray investigation, the values were 73.5° (model A) and 70.0° (model B). The results for the bond distances and bond angles did not vary significantly with this change in β .

The results obtained by least-squares refinement of model A with $\beta = 2^\circ$ are given in Table 4. Since the least-squares refinements were carried out with a diagonal weight matrix, the standard deviations have been corrected as described by Seip and Stølevik.²³

The most important non-bonded distances corresponding to the parameters in Table 4 are given in Table 5.

Only a few of all the mean amplitudes of vibration (u)²⁴ given as u^{obs} in Tables 4 and 5 were refined with the other parameters. The other values were fitted by additional refinements and by trial and error. To check that the values for the important distances were reasonable, tentative values were computed as described by Stølevik *et al.*²⁵ These values, which correspond to 300 °C, are included as u^{calc} in Tables 4 and 5, and the force constants used are given in Table 6. The agreement with the values used in the electron-diffraction study, seems quite satisfactory.

DISCUSSION

Table 4 shows that the average of the (C-C)_{ring} bonds is found 0.012 Å longer and

Table 4. Structural parameters for 2,2'-dichlorobiphenyl. The electron diffraction results (ED) were obtained by assuming rings with sixfold symmetry (Model A). The standard deviations given in parentheses apply to the last decimal place.

	ED $r_a(\text{Å})$ ²⁵	$u^{obs}(\text{Å})$	$u^{calc}(\text{Å})$	XD ^a $r(\text{Å})$		ED angles (degrees)	XD ^a angles (degrees)
(C-C) _{ring}	1.398(2)	0.042(3)	0.048	1.386 (average)			
Cl-C1'	1.495(9)	0.043(15)	0.052	1.493(5)	∠C1C2C1	121.4(9)	120.0(2)
C-Cl	1.732(4)	0.048(4)	0.055	1.748(3)	∠C1C6H6	125.5(35)	
C-H	1.095(10)	0.072	0.077	0.98	β	(2.0) ^b	2.3
					ϕ	73.5(20)	67-69

^a The distances corrected for thermal motion are given (X-ray diffraction). ^b β , the angle between the C-Cl bond and the ring plane, was not varied.

Table 5. Non-bonded distances and the corresponding mean amplitudes of vibration from electron diffraction. The mean amplitudes calculated with the force constants given in Table 6 are also given.

	$r_a(\text{\AA})$	$u^{\text{obs}}(\text{\AA})$	$u^{\text{calc}}(\text{\AA})$
C1...C3	2.42	0.062	0.060
C1...C4	2.80	0.069	0.066
C1...C2'	2.51	0.074	0.079
C1...C3'	3.79	0.072	0.078
C1...C4'	4.29	0.070	0.079
C2...C2'	3.24	0.152	0.138
C2...C3'	4.53	0.157	0.146
C2...C4'	5.14	0.142	0.138
C2...C5'	4.71	0.129	0.131
C2...C6'	3.48	0.120	0.121
C3...C3'	5.87	0.157	0.146
C3...C4'	6.50	0.133	0.125
C3...C5'	6.01	0.128	0.131
C4...C4'	7.09	0.115	0.098
C1...Cl2	2.74	0.076	0.078
C3...Cl2	2.70	0.085	0.079
C4...Cl2	4.00	0.085	0.079
C5...Cl2	4.53	0.082	0.080
C6...Cl2	4.03	0.086	0.078
C1...Cl2'	3.05	0.171	0.140
C2...Cl2'	3.38	0.245	0.209
C3...Cl2'	4.38	0.248	0.266
C4...Cl2'	4.98	0.252	0.283
C5...Cl2'	4.76	0.249	0.270
C6...Cl2'	3.86	0.238	0.219
Cl...Cl	3.58	0.314	0.296

the C—Cl bond 0.016 Å shorter in the X-ray than in the electron-diffraction investigation. The reason is probably a small shift in the centre of gravity of the carbon electrons relative to the nuclei towards the ring centre, giving a small systematic error in the X-ray results.

The molecule is found to be in a form closer to the *syn* than to the *anti* form both in the crystalline and in the gaseous state with a twist angle of about 70° in both cases. The twist angle found in the electron-diffraction investigation assuming planar chlorophenyl groups ($\beta=0$) of 75° (model A) or 72° (model B) may be compared with the X-ray result of 68.5° if the chlorine atoms are included in the definition of the least-squares planes. The assumption of $\beta=2^\circ$ in the electron-diffraction work gives a twist angle of 73.5° or 70.0° which may be compared to the result from the X-ray analysis of 66.8° between the least-squares planes through the carbon atoms of each ring. The difference of 3–7° found by the two methods may be real. A somewhat larger angle in the gaseous phase seems reasonable; the amplitude of torsional oscillation about the central bond is larger at the nearly 300°C higher temperature, and the oscillation is probably rather anharmonic, the Cl—Cl' separation being as small as 3.43 Å (in the solid). However, the twist angle is not well determined by the electron-diffraction method partly because of the large oscillations about the bridge bond

Table 6. Force constants used in the calculation of mean amplitudes of vibration. The number of contributions of each type is given in parentheses.

Stretching force constants (mdyn Å ⁻¹)		Repulsion force constants (mdyn Å ⁻¹)	
(C—C) _{ring}	5.40(12)	Cl...C3	0.45(12)
Cl—Cl'	4.60(1)	Cl...C4	0.20(6)
C—H	4.70(8)	Cl...H6	0.34(16)
C—Cl	3.40(2)	Cl...Cl	0.05(1)
Coupling constant (mdyn Å ⁻¹)		Torsional force constants (mdyn Å rad ⁻²)	
Cl—C2/C2—C3	0.75 (12)	C1C2C3C4	0.12(12)
Bending force constants (mdyn Å rad ⁻²)		C1C2C3H3	0.09(24) ^a
(CCC) _{ring}	0.70(12)	H3C3C4H4	0.07(12) ^a
Cl'ClC	0.90(4)	C2C1C1'C2'	0.08(4)
HCC	0.38(16)		
CICC	1.15(4)		

^a The torsional force constants of this type were assumed to be the same also in cases where the H atoms are replaced by C or Cl.

which gave a large u value for the Cl—Cl distance, and partly because the result depends somewhat on the assumptions about the bond angles.

In agreement with the investigation by Bastiansen,⁴ the electron-diffraction data give no evidence for more than one conformer even at 300 °C. The amount of a possible second form which can be introduced without destroying the agreement between experimental and theoretical curves, depends on the ϕ angle assumed for the second form. The RD function for a form with $\phi \approx 105^\circ$ does not differ drastically from the function shown in Fig. 3, and up to 25 % of a form of this kind might be difficult to detect. However, a somewhat larger ϕ value is more probable, and changing ϕ to about 120° (cf. Table 1) gives a considerable change in the RD curve. If this ϕ value is correct an upper limit for a second conformer seems to be about 15 %.

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