ring skeleton, *i.e.* the lengthening of the bond C(2)—C(2^{i}), can be viewed as contributing to the relaxation of a repulsive interaction between the substituents. In view of the results of cyclopropanecarbonitrile (Kiers *et al.*, 1985), the effects of cyano substituents on the cyclopropane structure are approximately additive, but do not solely depend on topology, but also on the stereochemistry of the individual molecule.

This latter aspect is expected to be even more important for cyclopropanes multiply substituted by carbonyl groups, which additionally introduce several conformational degrees of freedom. We are currently investigating the cumulative effect of halogen substituents on the geometry of the cyclopropane moiety in order to test whether the findings of the present investigation can be transferred to substituents that are not π acceptors.

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Substituted Cyclopropanes. 2.* *cis*-1,2,3-Trichlorocyclopropane

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Abstract. $C_3H_3Cl_3$, $M_r = 145{\cdot}42$, orthorhombic, $Pnma$, $a = 10{\cdot}237\,(3)$, $b = 8{\cdot}665\,(2)$, $c = 6{\cdot}220\,(2)$ Å, $V = 551{\cdot}7$ Å^3, $Z = 4$, $D_x = 1{\cdot}75$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}15$ mm^{-1}, $F(000) = 288$, $T = 293$ K, $R = 0{\cdot}038$ for 558 unique observed reflections. The molecule displays symmetry close to the ideal C_{3v}; crystallographic mirror symmetry is imposed. The mean ring bond length (corrected for libration) is 1·504 Å; the chlorine substituents thus appear to have little effect on this parameter.

Introduction. In the last few years, there has been considerable progress in understanding the nature of bonding in, and its implication for the geometry of,

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* Part 1: Jones & Schrumpf (1987).

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substituted cyclopropanes. A qualitative picture of the origin of cyclopropane asymmetry induced by different substituents has been given by Hoffmann using molecular-orbital arguments based on the Walsh model (Hoffmann, 1970). According to this interpretation, strong π-electron acceptors are expected to shorten the bond opposite the substituent and lengthen the adjacent ones. Conversely, good π-electron donors should lengthen all bonds of the ring. These ideas were supported by most of the experimental data at that time. However, it had been pointed out that saturated substituents such as halogen atoms or the amino group did not fit the general pattern (Gillies, 1976; Harmony, Bostrom & Hendricksen, 1975); electron flow from the halogen lone pairs to the $1a_2'$ or the $4e'$ Walsh orbitals should lengthen the bonds adjacent to the substituent. This prediction did not agree well with the experimental data.

Recently, it has been shown by *ab initio* Hartree–Fock calculations with geometry optimization that quite good predictions of experimental geometries are possible (Skancke, 1977; Skancke & Boggs, 1978, 1979*a,b*) and may even reveal errors in experimental data (Hedberg, Hedberg & Boggs, 1982). The interaction of halogen substituents with the cyclopropane ring on the basis of the *ab initio* results is interpreted as follows. Fluorine as a strong σ-electron acceptor withdraws electrons from the ring without back-donating π electrons. This results in the marked shortening of the lateral CC bonds in 1,1-difluorocyclopropane (Perretta & Laurie, 1975) and an average ring bond length similar to that in cyclopropane (Bastiansen, Fritsch & Hedberg, 1964; Butcher & Jones, 1973). This is in agreement with the observation that the CC ring bonds in *cis*-1,2,3-trifluorocyclopropane (Gillies, 1976) are only slightly shorter than those of cyclopropane.

The CC bond lengths in chlorocyclopropane are about the same as in cyclopropane, *i.e.* no appreciable asymmetry is induced (Schwendeman, Jacobs & Krigas, 1964). This is interpreted as the result of the opposing effects of σ-electron withdrawal and π-electron donation. From an *ab initio* study of 1,1-dichlorocyclopropane (Hedberg, Hedberg & Boggs, 1982) it was concluded that, on geminal disubstitution by chlorine, π-electron density is not transferred to the ring, but rather to a region between the two chlorine atoms. Consequently, as in 1,1-difluorocyclopropane, only the electron-withdrawing mechanism is operative, lengthening the bond opposite the apical carbon [1·535 (9) Å] considerably compared with chlorocyclopropane. The average CC bond distance [1·508 (3) Å] is only slightly less than in cyclopropane itself.

It would be interesting now to study the structural consequences of vicinal disubstitution by chlorine. To our knowledge, there are no published structural data on simple suitably substituted chlorocyclopropanes; thus, we have undertaken an X-ray study on *cis*-1,2,3-trichlorocyclopropane, one of the two chlorocyclopropanes solid at ambient temperatures.

Table 1. *Atom coordinates* ($\times 10^4$) *and isotropic temperature factors* (Å$^2 \times 10^3$)

	x	y	z	U/U_{eq}
Cl(1)	6080 (1)	2500	6527 (2)	70 (1)*
Cl(2)	6520 (1)	4387 (1)	2040 (1)	60 (1)*
C(1)	4894 (4)	2500	4559 (6)	49 (1)*
C(2)	5089 (2)	3359 (3)	2504 (4)	46 (1)*
H(1)	4128 (35)	2500	5017 (63)	49 (10)
H(2)	4380 (25)	3824 (29)	1926 (34)	38 (6)

* Equivalent isotropic U calculated from anisotropic U.
$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

Table 2. *Bond lengths* (Å) *and angles* (°)

	Uncorrected	Corrected
C(1)–Cl(1)	1·724 (5)	1·741
C(1)–C(2)	1·492 (5)	1·506
C(2)–C(2^i)	1·489 (6)	1·501
C(2)–Cl(2)	1·739 (3)	1·754
C(2)–C(1)–C(2^i)	59·9 (3)	
Cl(2)–C(2)–C(1)	120·7 (3)	
Cl(2)–C(2)–C(2^i)	120·8 (2)	
C(1)–C(2)–C(2^i)	60·1 (2)	
Cl(1)–C(1)–C(2)	120·9 (3)	

Symmetry operator: (i) $x, 0·5-y, z$.

Experimental. *cis*-1,2,3-Trichlorocyclopropane has recently been prepared from *cis*-1,2,3,3-tetrachlorocyclopropane (Schrumpf & Bergholz, 1983). The material used in the present study was prepared by the stepwise controlled partial reduction of hexachlorocyclopropane by tri-*n*-butylstannane. Crystals in the form of colourless prisms were obtained by diffusion of water into a saturated solution in glacial acetic acid.

Crystal 0·25 × 0·2 × 0·2 mm. 1947 profile-fitted intensities (Clegg, 1981) recorded on a Stoe–Siemens four-circle diffractometer. Monochromated Mo $K\alpha$ radiation, $2\theta_{\max}$ 55°; octants $+h+k+l$, $+h-k-l$, $-h-k-l$. Three check reflections, no intensity change. $R_{\rm int}$ 0·021 for 672 unique reflections (index ranges after merging $|h| \leq 13$, $|k| \leq 11$, $|l| \leq 8$), 558 with $F > 4\sigma(F)$ used for all calculations (program system *SHELXTL*; Sheldrick, 1978). Cell constants refined from 2θ values of 48 reflections in the range 20–23°. No absorption correction.

Structure solution by routine direct methods. Refinement on F to R 0·038, wR 0·041 [non-H atoms anisotropic, H atoms isotropic; 39 parameters], weighting scheme $w^{-1} = \sigma^2(F) + 0·0002F^2$; $S = 1·6$, slope of normal probability plot 1·4; extinction correction of the form $F_{\rm corr} = F_c(1 + xF_c^2/\sin 2\theta)^{-0·25}$ with $x = 3·2\ (3) \times 10^{-5}$. Max. Δ/σ 0·002. Max. and min. heights in final $\Delta\rho$ map $\pm 0·38$ e Å^{-3}. Atomic scattering factors as incorporated in *SHELXTL*.

Discussion. Final atomic coordinates and derived parameters are given in Tables 1 and 2.* The bond lengths were subjected to a rigid-body libration correction (Schomaker & Trueblood, 1968), for which $R_{\text{libr}} = 0{\cdot}023$.

A crystallographic mirror plane passes through C(1), Cl(1) and H(1) (see Fig. 1); however, the non-crystallographic symmetry of the title molecule is close to the expected C_{3v}. The mean bond length corrected for libration (Table 2) is 1·504 Å. This is close to the gas-phase value of cyclopropane (1·510 Å, Bastiansen *et al.*, 1964) and to the average CC ring bond lengths of 1·510 (2) Å found in a survey of the geometry of over 88 cyclopropane derivatives (Allen, 1980).

Our result implies that either (*a*) there is a fortuitous cancelling of lengthening and shortening effects on the ring bonds on multiple vicinal substitution by chlorine as in the title molecule or (*b*) there is no net effect on the ring bonds by any of the chlorine substituents, as in the monosubstituted cyclopropane. From the present data alone, one cannot decide between these alternatives. The structures of the two isomers of 1,2-dichlorocyclopropane might be helpful in this matter, because vicinal disubstitution reinforces the substituent action, if any, on the unique bond. An electron diffraction study of these two molecules is under way.

The present result is in accord with the microwave data on *cis*-1,2,3-trifluorocyclopropane (Gillies, 1976) showing ring bonds also only slightly shorter than in cyclopropane.

The average CCl bond length found in this study is 1·750 Å. This is in good agreement with the corresponding gas phase values of chlorocyclopropane [1·740 (11) Å, Schwendeman *et al.*, 1964] and 1,1-dichlorocyclopropane [1·756 (2) Å, Hedberg *et al.*, 1982].

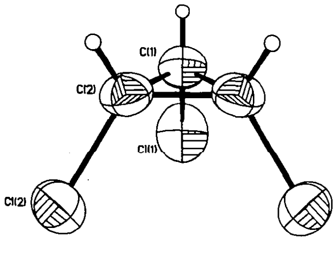

Fig. 1. Thermal-ellipsoid plot (50% level) of the title molecule, showing the atom-numbering scheme. H-atom radii arbitrary.

cis-Substituents attached to a cyclopropane ring are expected to interact because of their relatively short interatomic distances. In the title molecule, the Cl···Cl non-bonded distance is 3·30 Å, whereas the sum of the van der Waals radii of the chlorine atoms is 3·60 Å (Pauling, 1960), which is also the smallest intermolecular distance found in the title compound (see Fig. 2 for a view of the crystal packing). This means a certain penetration of the valence electron clouds on vicinal chlorine substituents. Interestingly, the angle of inclination of the chlorine substituents towards the ring plane in trichlorocyclopropane (54°) is only 2° smaller than in monochlorocyclopropane (56°; Schwendeman *et al.*, 1964). This allows a Cl···Cl relaxation of *ca* 0·1 Å compared with a hypothetical trichlorocyclopropane molecule without angle strain, *i.e.* with an angle of inclination of the chlorine substituents as in chlorocyclopropane.

There are only four possibilities for relaxing the non-bonded strain available to the present molecule: two bond-length (CC and CCl) and one angle (CCCl) relaxations or a transition to a structure of lower symmetry. Since the symmetry of the free molecule is conserved to a first approximation and the bond lengths of the heavy atoms are identical with those of the monosubstituted cyclopropane, only the opening of the CCCl bond angle remains. The small observed change in this bond angle on going from the mono- to the trisubstituted cyclopropane would be consistent with a large force constant of the HCCl rocking coordinate in the title molecule; values for this force constant are not known in this type of molecule (Schrumpf & Dunker, 1985).

Alternatively, there might be a very shallow valley of the potential between non-bonded chlorine atoms. The classical picture of non-bonded interactions, which associates the penetration of the spheres defined by the respective van der Waals radii with a steep rise in potential energy of the molecular system, may hold for situations where non-bonded atoms approach in such a way that their *n*-electron clouds point to each other. In

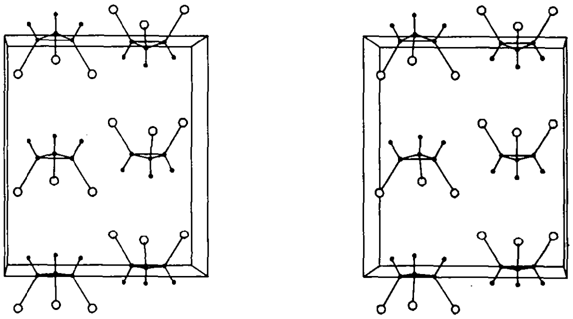

Fig. 2. Stereographic packing diagram viewed down the *z* axis (*y* across, *x* up). Open circles, Cl; black dots, C and H.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43714 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the title molecule, the C—Cl bond vectors have large parallel components, thus permitting the interaction of halogen lone pairs with antibonding σ^* orbitals. This is the interpretation of the '*cis*' effect, *i.e.* the greater stability of (*Z*)-1,2-dihalogenoethenes compared with their (*E*)-diastereomers (Craig, Piper & Wheeler, 1971; Epiotis, 1973; Epiotis & Yates, 1976). However, this view is not unchallenged (Bingham, 1976). The results of recent *ab initio* calculations on the two 1,2-difluoroethenes have been interpreted in the sense of through-bond destabilization of the (*E*)-isomer relative to the (*Z*)-isomer rather than attractive interaction between the *cis* fluorine atoms (Skancke & Boggs, 1979*a*). However, whereas the origin of the interaction is still open to discussion, the validity of the hard-sphere model for rationalizing non-bonded interaction between two vicinal halogen substituents must be questioned. This potential appears to be strongly dependent (even to the extent of changing sign) on the relative orientation of the bond vectors. This problem will be further pursued in our laboratories.

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Substituted Cyclopropanes. 3.* Hexachlorocyclopropane (Redetermination)

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Abstract. C_3Cl_6, $M_r = 248\cdot75$, monoclinic, $P2_1/c$, $a = 10\cdot899\ (4)$, $b = 6\cdot190\ (2)$, $c = 12\cdot682\ (5)$ Å, $\beta = 112\cdot13\ (2)°$, $V = 792\cdot5$ Å^3, $Z = 4$, $D_x = 2\cdot08$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0\cdot2$ mm^{-1}, $F(000) = 480$, $T = 293$ K, $R = 0\cdot045$ for 1199 unique observed reflections. The mean libration-corrected C—C bond length is 1·537 Å, appreciably longer than in *cis*-1,2,3-trichlorocyclopropane (1·504 Å). It is suggested that this is a result of repulsive non-bonding Cl···Cl interactions.

Introduction. We have determined the crystal structure of *cis*-1,2,3-trichlorocyclopropane (Schrumpf & Jones, 1987*a*) to study the effect of vicinal substituents on the geometry of the cyclopropane ring. This study was undertaken because substitution by one chlorine substituent does not change the geometry of the cyclopropane ring (Schwendeman, Jacobs & Krigas, 1964),

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* Part 2: Schrumpf & Jones (1987*a*).