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-difluoro-ethenes 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, 1979a). 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, $M_r = 248.75$, monoclinic, $P2_1/c$, $a = 10.899$ (4), $b = 6.190$ (2), $c = 12.682$ (5) Å, $\beta = 112.13$ (2)°, $V = 792.5$ Å^3, $Z = 4$, $D_x = 2.08$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.2$ mm^{-1}, $F(000) = 480$, $T = 293$ K, $R = 0.045$ 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, 1987a) 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 (1987a).

while geminal disubstitution induces a large asymmetry of the ring CC bonds ($\Delta r = 0.041$ Å, Hedberg, Hedberg & Boggs, 1982) which is rather unexpected. Thus, it was of interest to study the effect of vicinal disubstitution by chlorine on the cyclopropane geometry.

In view of the anticipated steric crowding on one of the faces of the cyclopropane ring in cis-1,2,3-trichlorocyclopropane, one might expect some geometrical relaxation by bond lengthening and bond-angle opening. Surprisingly, the structure of trichlorocyclopropane does not reflect any appreciable relief of the anticipated steric pressure; on the contrary, the ring CC bonds were found to be marginally shorter (1.504 Å) than those in gaseous cyclopropane (1.510 Å; Bastiansen, Fritsch & Hedberg, 1964).

We interpreted these observations by assuming that the three vicinal chlorine atoms shorten the ring CC bonds by an electronic interaction of the kind proposed by Hoffmann (1970), and that the potential-energy curve of the steric interaction might have a very shallow valley for the particular C—Cl bond vector orientation present in that molecule. We could not even exclude an attractive interaction between the chlorine substituents.

In order to test the hypothesis of non-bonded attractive forces between chlorine substituents, more data on simple chlorocyclopropanes are desirable. In the family of the chloro-substituted cyclopropanes, only the symmetrical tri- and hexachloro derivatives are solids at room temperature. Hexachlorocyclopropane has previously been investigated by gas-phase electron diffraction (Barzdain, Gracheva & Alekseev, 1972); the CC bond distance of 1.513 (9) Å implies the absence of any appreciable influence of chlorine substitution on the cyclopropane geometry. Because of the relatively large error of the bond lengths given in the electron diffraction work and since we wanted to have another solid-state structure to compare with our previous crystal data, we studied the structure of hexachlorocyclopropane by X-ray crystallography. A preliminary report of this structure has been published (Takano, Chiba, Sasada, Kakudo, Nozakura & Murahahi, 1965) but with no coordinates or molecular dimensions.

Experimental. Hexachlorocyclopropane was synthesized by the method of Tobey & West (1966). Crystals in the form of colourless prisms were obtained by diffusing water into a saturated solution in glacial acetic acid.

Crystal $0.4 \times 0.27 \times 0.23$ mm. 3611 profile-fitted intensities (Clegg, 1981) recorded on a Stoe–Siemens four-circle diffractometer. Monochromated Mo $K\alpha$ radiation, $2\theta_{max}$ 55°; hemisphere $\pm h \pm k + l$. Three check reflections, no significant intensity change. R_{int} 0.031 for 1813 unique reflections (index ranges after merging $|h| \le 14$, $|k| \le 8$, $|l| \le 16$), 1199 with $F > 4\sigma(F)$ used for all calculations (program system

SHELXTL; Sheldrick, 1978). Cell constants refined from 2θ values of 45 reflections in the range 20–23°. No absorption correction (no improvement of R_{int} of 400 azimuthal scan data).

Structure solution by assumed isostructurality with C_3Br_6 (Schrumpf & Jones, 1987b). Refinement on F to R 0.045, wR 0.043 [82 parameters, weighting scheme $w^{-1} = \sigma^2(F) + 0.0001F^2$, $S = 1.54$, slope of normal probability plot 1.34]. Max. Δ/σ 0.003. Max. and min. heights in final $\Delta\rho$ map +0.33, −0.4 e Å^{-3}. Atomic scattering factors as incorporated in SHELXTL.

Discussion. Final atomic coordinates and derived molecular dimensions are presented in Tables 1 and 2.* A view of the molecule is given in Fig. 1; Fig. 2 is a packing diagram. The bond lengths were corrected for libration by the rigid-body method of Schomaker & Trueblood (1968); $R_{libr} = 0.034$.

No crystallographic symmetry is imposed on the molecule of the title compound, but it is effectively of D_{3h} symmetry and can be described by three averaged parameters only, the CC and CCl bond distances and the ClCCl bond angle. The CCl bond length and the bond angle are similar in the crystalline state (1.747 Å and 112.2°, respectively) and the vapour (1.734 Å and 112°; Barzdain et al., 1972). However, the CC bond lengths differ by 0.024 Å, which is three to four e.s.d.'s. This may be a packing effect, although in general these tend to decrease bond distances. Alternatively, the error in the electron diffraction study could be larger than estimated by the authors, as (1) only a limited number of diffraction intensity data points (not exceeding 24 Å^{-1}) were available, (2) the least-squares fitting was not performed on the molecular intensity distribution itself, (3) the grid steps might have been too large, (4) no shrinkage effect was taken into account. This might also explain the large divergence factor of 0.12 given by the Russian workers.

Irrespective of the reason for the discrepancy between gas-phase and solid-state results, the difference between the mean solid-state CC bond lengths in the trichloro (1.504 Å) and the hexachloro (1.537 Å) derivatives is obvious. In addition, there is a distinct lengthening of the CC bonds in the title molecule relative to cyclopropane (1.510 Å in the vapour phase; Bastiansen et al., 1964).

If the trichloro derivative may be regarded as a superposition of three monochlorocyclopropanes – at least as far as the effect of the substituents on the cyclopropane ring geometry is concerned – the CC bond length in the hexachloro compound might be

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

	x	y	z	U_{eq}*
Cl(11)	675 (1)	2679 (2)	3456 (1)	59 (1)
Cl(12)	1152 (1)	2356 (2)	5834 (1)	56 (1)
Cl(21)	2279 (1)	7148 (2)	3927 (1)	70 (1)
Cl(22)	2762 (1)	6772 (2)	6305 (1)	66 (1)
Cl(31)	3797 (1)	2667 (2)	4037 (1)	62 (1)
Cl(32)	4286 (1)	2332 (2)	6421 (1)	57 (1)
C(1)	1740 (3)	3287 (6)	4834 (3)	35 (1)
C(2)	2505 (3)	5413 (5)	5048 (3)	37 (1)
C(3)	3228 (3)	3281 (6)	5105 (3)	37 (1)

* Equivalent isotropic U calculated from anisotropic U:

$$U_{eq} = \tfrac{1}{3}\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

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

	Uncorrected	Corrected
C(1)–Cl(11)	1·736 (4)	1·751
C(1)–Cl(12)	1·721 (5)	1·735
C(2)–Cl(21)	1·724 (5)	1·740
C(2)–Cl(22)	1·729 (5)	1·745
C(3)–Cl(31)	1·731 (5)	1·746
C(3)–Cl(32)	1·735 (4)	1·750
C(1)–C(2)	1·527 (6)	1·538
C(1)–C(3)	1·527 (6)	1·535
C(2)–C(3)	1·525 (6)	1·537

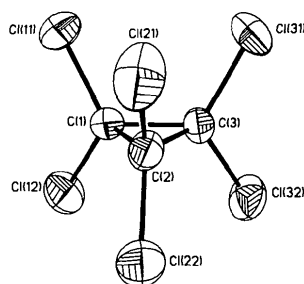|			
Cl(11)–C(1)–Cl(12)	112·1 (3)	Cl(11)–C(1)–C(2)	118·6 (4)
Cl(12)–C(1)–C(2)	119·2 (4)	Cl(11)–C(1)–C(3)	118·5 (4)
Cl(12)–C(1)–C(3)	119·5 (3)	C(2)–C(1)–C(3)	59·9 (3)
Cl(21)–C(2)–Cl(22)	112·4 (3)	Cl(21)–C(2)–C(1)	119·4 (3)
Cl(22)–C(2)–C(1)	118·2 (4)	Cl(21)–C(2)–C(3)	119·2 (4)
Cl(22)–C(2)–C(3)	118·4 (3)	C(1)–C(2)–C(3)	60·0 (3)
Cl(31)–C(3)–Cl(32)	112·0 (3)	Cl(31)–C(3)–C(1)	119·2 (3)
Cl(32)–C(3)–C(1)	118·8 (4)	Cl(31)–C(3)–C(2)	119·0 (4)
Cl(32)–C(3)–C(2)	118·8 (4)	C(1)–C(3)–C(2)	60·0 (3)

Fig. 1. Thermal-ellipsoid plot (50% level) of the title molecule, showing the atom-numbering scheme.
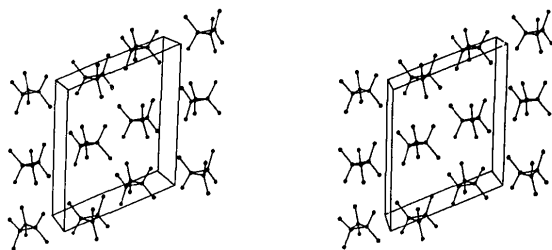
Fig. 2. Stereo packing plot viewed approximately parallel to the *y* axis.

considered to be the result of the action of three 1,1-dichlorocyclopropanes. In the latter molecule, the average ring bond distance (1·508 Å; Hedberg *et al.*, 1982) is nearly identical to that of cyclopropane and monochlorocyclopropane. Assuming additivity of the effect of three geminal chlorine pairs, one expects no net bond-length change in hexachlorocyclopropane. Thus, the observed lengthening in the latter molecule must be due to some other effect.

In the absence of *ab initio* calculations, we would offer the following classical explanation. The addition of three further chlorine substituents to trichlorocyclopropane is associated with a buttressing effect opposing the CCCl bond-angle opening observed in trichlorocyclopropane relative to monochlorocyclopropane. This results in the observed increase of the angle of inclination of the chlorine substituents towards the ring plane by almost 2°. Concomitantly, the non-bonded distances between the vicinal chlorine atoms decrease by 0·1 Å. Provided that, at this distance of 3·22 Å (av.), we move on the repulsive side of the energy curve for non-bonded interactions, the energy rise is partially offset by a bond lengthening of the ring CC bonds by 0·023 Å.

This interpretation is admittedly very crude and ignores electronic interactions particular to the special bonding situation in cyclopropanes, but we would nevertheless suggest that the observed increase of the CC bond distances within the ring is of steric origin. The breakdown of this into different energy components and into contributions originating from particular orbitals should be a rewarding objective of an *ab initio* calculation of the title molecule.

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