Crystal and Molecular Structure of *cis*-6-Chloro-*trans*-7-chloro-*cis*-bicyclo[3,2,0]heptan-2-one

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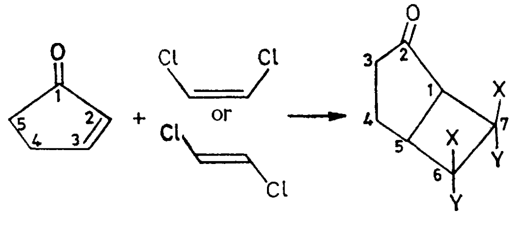
The major product of photocycloaddition of *cis*-dichloroethylene to 2-cyclopentenone is established by a single-crystal *X*-ray diffraction study to be *cis*-6-chloro-*trans*-7-chloro-*cis*-bicyclo[3,2,0]heptan-2-one. The configuration found is consistent with the suggestions that photoaddition begins at C(3) of the ketone and that rotational equilibration of the diradical intermediates is completed before ring closure.

This isomer of $C_7H_8Cl_2O$ crystallizes in space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions $a = 6{\cdot}191$, $b = 11{\cdot}172$, $c = 11{\cdot}709$(Å), and $\beta = 94{\cdot}73°$. The structure was solved from diffractometer data by reiterative application of Sayre's equation and refined by full-matrix least-squares to *R* 0·056 for the 1236 reflections above background. Both the four- and five-membered rings are markedly nonplanar.

THE products of the two-step photocycloaddition of 2-cyclopentenone to *cis*- and *trans*-dichloroethylenes are isomeric 6,7-dichlorobicyclo[3,2,0]heptan-2-ones. The distribution of products suggests that the initial bond to the ketone in the photoaddition reaction forms at C(3), and that the diradical intermediates are rotationally equilibrated before ring closure.[1] This interpretation, of course, depends on the correct identification of the product isomers.[1] The major product of photocycloaddition with *cis*-dichloroethylene was initially identified as (III) by n.m.r. methods.[1]



	X-6(*cis*)	X-7(*cis*)	Y-6(*trans*)	Y-7(*trans*)
(I)	H	H	Cl	Cl
(II)	H	Cl	Cl	H
(III)	Cl	H	H	Cl
(IV)	Cl	Cl	H	H

The single-crystal *X*-ray diffraction study reported here was undertaken to confirm this result. In addition, we believe the molecular geometry of a bicyclo[3,2,0]-heptane derivative may be of interest since this system has been previously described only as a fragment of a larger system of fused rings.[2,3]

Description of the Structure.—The *X*-ray diffraction results confirm that the product is indeed (III) (Figure 1), a bicyclo[3,2,0]heptan-2-one with *cis*-ring fusion at C(1) and C(5), and with Cl(6) *cis* (or *endo*) and Cl(7) *trans* (or *exo*). Neither ring is planar. The five-membered ring has an envelope conformation where C(3), C(4), and C(5) form a ' flap ' making a dihedral angle of 153·3° with a least-squares plane through C(1), C(2), C(3), C(5), and O. (The latter five atoms are nearly coplanar.) The envelope is folded so that the flap is bent in the *endo*-

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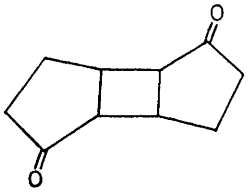
[1] W. L. Dilling, T. E. Tabor, F. P. Boer, and P. P. North, *J. Amer. Chem. Soc.*, 1970, **92**, 1399.

[2] T. N. Margulis, *Acta Cryst.*, 1965, **18**, 724.

[3] Y. Okaya and A. Bednowitz, *Acta Cryst.*, 1967, **22**, 111; J. Carnduff, J. Iball, D. G. Leppard, and J. N. Low, *Chem. Comm.*, 1969, 1218.

direction. By puckering, the ring relieves eclipsing interactions between hydrogens on C(3) and C(4). This conformation differs somewhat from that found in tricyclo[5,3,0,$0^{2,6}$]decane-3,8-dione [2] (V), the centrosymmetric photodimer of cyclopentenone. In compound (V), which has a planar four-membered ring, the carbon atoms analogous to C(4) and C(5) are respectively 0·45 and 0·21 Å above the plane formed by C(2) and its three substituents,[2] whereas, in the conformation adopted by (III), C(4) is 0·38 above and C(5) 0·04 Å below this plane.



(V)

(The equation of the best least-squares plane through C(1)—(3) and O is $5{\cdot}633x + 0{\cdot}377y - 5{\cdot}702z = -1{\cdot}268$).

The dihedral angle in the four-membered ring is 149·3°, with the ring bent in a direction which relieves a possible interaction between Cl(6) and H(4B) (Figure 1). The Cl(6) · · · H(4B) intramolecular contact is 2·816 Å. The value of the dihedral angle is fairly typical for puckered cyclobutanes.[4]

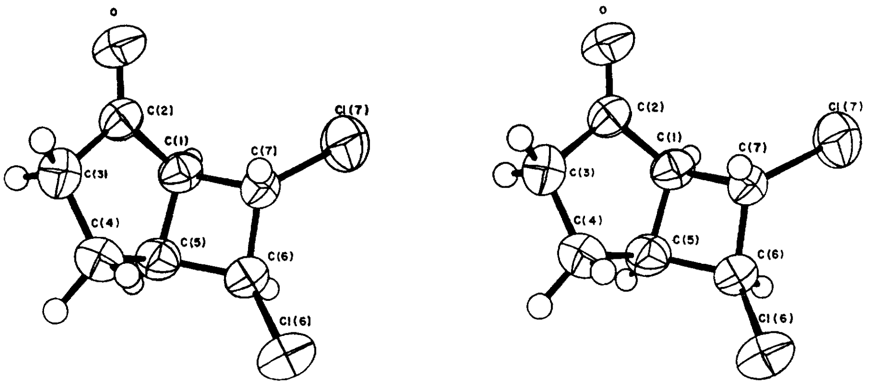


FIGURE 1 Stereodiagram of the molecule with the ellipsoids of thermal motion drawn at 50% probability (root-mean-square displacements along the principal axes are given in Table 3)

Bond angles (Table 1) in the five-membered ring range between 104·8 and 108·1°. The largest of these values, that for C(2), is considerably less than the 120° angle ' normal ' for sp^2 hybridized carbon. Bond angles in the four-membered ring are all between 87·3 and 88·2°, with errors of ±0·3°. On the other hand, the bridgehead angles C(2)–C(1)–C(7) (114·2°) and C(4)–C(5)–C(6) (117·1°) are considerably larger than normal tetrahedral angles, as are the C–C–Cl angles (116·7—120·1°).

There is considerable interest [2,4] in cyclobutane structures because of the long C–C single bonds reported for some of these molecules. However, the bond distances (Table 2) in the present structure (1·537, 1·538, 1·512, and 1·550 Å, all ±0·005 Å), do not appear to be significantly elongated beyond the standard [5] C–C single bond distance of 1·541 Å. Bond lengths in the five-membered ring are similarly normal, as are the C=O and C–Cl distances.[5] The chlorine atoms show fairly large and anisotropic amplitudes of thermal motion. These are illustrated as

TABLE 1

Bond angles (deg.)*

C(2)–C(1)–C(5)	106·8(3)	C(4)–C(5)–C(1)	104·8(3)
C(2)–C(1)–C(7)	114·2(3)	C(4)–C(5)–C(6)	117·1(3)
C(2)–C(1)–H(1)	117·0(21)	C(4)–C(5)–H(5)	105·8(27)
C(5)–C(1)–C(7)	87·3(3)	C(1)–C(5)–C(6)	87·7(3)
C(5)–C(1)–H(1)	116·7(21)	C(1)–C(5)–H(5)	120·4(28)
C(7)–C(1)–H(1)	111·2(23)	C(6)–C(5)–H(5)	120·0(29)
C(1)–C(2)–C(3)	108·1(3)	C(5)–C(6)–Cl(6)	120·1(3)
O–C(2)–C(3)	126·0(3)	C(5)–C(6)–C(7)	88·6(3)
C(1)–C(2)–O	125·8(3)	C(5)–C(6)–H(6)	111·6(29)
		Cl(6)–C(6)–C(7)	116·7(3)
C(2)–C(3)–C(4)	106·6(3)	Cl(6)–C(6)–H(6)	107·1(29)
C(2)–C(3)–H(3A)	108·2(41)	C(7)–C(6)–H(6)	111·9(31)
C(2)–C(3)–H(3B)	106·2(23)		
C(4)–C(3)–H(3A)	107·7(39)	C(6)–C(7)–Cl(7)	118·2(3)
C(4)–C(3)–H(3B)	115·8(23)	C(6)–C(7)–C(1)	88·2(3)
H(3A)–C(3)–H(3B)	112·0(47)	C(6)–C(7)–H(7)	114·3(22)
		Cl(7)–C(7)–C(1)	118·6(3)
C(3)–C(4)–C(5)	106·1(3)	Cl(7)–C(7)–H(7)	105·8(20)
C(3)–C(4)–H(4A)	113·9(26)	C(1)–C(7)–H(7)	111·4(19)
C(3)–C(4)–H(4B)	111·6(22)		
C(5)–C(4)–H(4A)	110·2(25)		
C(5)–C(4)–H(4B)	114·6(21)		
H(4A)–C(4)–H(4B)	100·7(33)		

* Throughout these Tables standard errors, in parentheses, were calculated from the variance–covariance matrix in the final least-squares cycle (ref. 6).

TABLE 2

Bond distances (Å)

C(1)–C(2)	1·501(5)	C(1)–H(1)	1·14(4)
C(2)–C(3)	1·510(5)	C(3)–H(3A)	0·87(6)
C(3)–C(4)	1·493(6)	C(3)–H(3B)	1·07(4)
C(4)–C(5)	1·531(6)	C(4)–H(4A)	1·06(5)
C(5)–C(1)	1·537(5)	C(4)–H(4B)	1·00(4)
C(5)–C(6)	1·538(5)	C(5)–H(5)	0·89(5)
C(6)–C(7)	1·512(5)	C(6)–H(6)	0·97(5)
C(7)–C(1)	1·550(5)	C(7)–H(7)	1·04(4)
C(2)–O	1·201(4)		
C(6)–Cl(6)	1·771(4)		
C(7)–Cl(7)	1·772(4)		

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[4] B. Greenberg and B. Post, *Acta Cryst.*, 1968, **B24**, 918.

[5] *Chem. Soc. Special Publ.*, No. 11, 1958.

thermal ellipsoids[6] (50% probability) in Figure 1 and as root-mean-square displacements in Table 3 (calculated by a program described in ref. 7).

TABLE 3

Root-mean-square displacements along principal axes *

	Axis (1)	Axis (2)	Axis (3)
Cl(6)	0·204(2)	0·311(2)	0·345(2)
Cl(7)	0·207(2)	0·292(2)	0·386(2)
O	0·207(4)	0·263(3)	0·289(3)
C(1)	0·214(4)	0·228(4)	0·241(4)
C(2)	0·200(4)	0·232(4)	0·240(4)
C(3)	0·220(5)	0·254(5)	0·292(5)
C(4)	0·223(5)	0·251(5)	0·323(5)
C(5)	0·208(5)	0·242(4)	0·269(5)
C(6)	0·198(5)	0·262(5)	0·267(5)
C(7)	0·200(4)	0·218(4)	0·259(4)

* Ordered on increasing magnitude.

The crystals pack (Figure 2)[6] with the carbonyl dipoles aligned parallel to y and opposed along centres of symmetry. The closest C · · · O and C · · · C intermolecular distances (3·250 and 3·584 Å) (Table 4), arise from this type of interaction. The four-membered rings are oriented approximately parallel to the xy plane. A remarkable feature of the packing is that all but one of the intermolecular contacts <4 Å (Table 4) involve either the oxygen atom or Cl(6).

TABLE 4

Intermolecular contacts <4 Å, excluding those involving hydrogen

Cl(6) · · · Cl(7^{I})	3·645	O · · · O^{VII}	3·341
Cl(6) · · · C(4^{II})	3·788	O · · · C(6^{VI})	3·370
Cl(6) · · · O^{III}	3·886	O · · · C(3^{VI})	3·434
Cl(6) · · · Cl(7^{IV})	3·901	O · · · C(3^{VIII})	3·449
Cl(6) · · · C(4^{V})	3·950	O · · · C(4^{VI})	3·785
Cl(6) · · · C(5^{V})	3·994	O · · · C(1^{VI})	3·848
O · · · C(2^{VI})	3·250	C(2) · · · C(2^{VI})	3·584
O · · · C(7^{VI})	3·319		

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $-1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
II $-x, 1 - y, 1 - z$
III $-x, \frac{1}{2} + y, \frac{1}{2} - z$
IV $x, \frac{1}{2} - y, \frac{1}{2} + z$
V $x - 1, y, z$
VI $-x, -y, 1 - z$
VII $-x, y - \frac{1}{2}, \frac{1}{2} - z$
VIII $1 - x, -y, 1 - z$

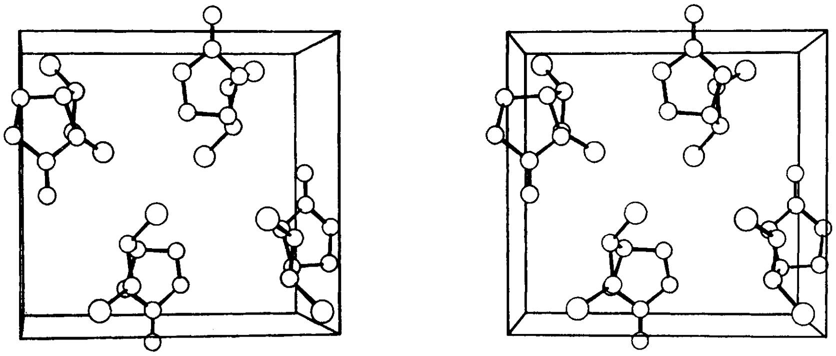

FIGURE 2 Molecular packing in a unit cell of the molecule. The z axis is horizontal and y is vertical

EXPERIMENTAL

Crystal Data.—$C_7H_8Cl_2O$, $M = 179{\cdot}13$, $a = 6{\cdot}191 \pm 0{\cdot}005$, $b = 11{\cdot}172 \pm 0{\cdot}008$, $c = 11{\cdot}709 \pm 0{\cdot}008$ Å, $\beta = 94{\cdot}73(4)°$, $U = 807{\cdot}0$ Å^3, $D_m = 1{\cdot}47$, $Z = 4$, $D_c = 1{\cdot}474$, $F(000) = 400$. Space group $P2_1/c$ (C^5_{2h}) from systematic absences: $h0l$ for l odd and $0k0$ for k odd. Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å; μ(Mo-K_α) = 7·19 cm^{-1}. The crystal used in the present study, of dimensions *ca.* 0·77 × 1·00 × 2·28 mm, was cleaved with a razor from a large irregular specimen, and was carefully centred on a Picker four-circle automatic goniostat, with its long dimension (parallel to [011]) collinear with ϕ. Lattice constants were calculated by least-squares refinement of the setting angles of 11 reflections. The intensities of 1375 reflections were measured by use of the θ—2θ scan mode and Mo-K_α radiation selected using the (100) reflection of a highly oriented graphite crystal monochromator. A 4° take-off angle was used, and a detector aperture 6·0 mm square was placed 30 cm from the crystal. Scan angles were from 2·2—2·5° over the range 0—50° of 2θ examined. Attenuators were used to prevent the count rate exceeding 12,000 s and the scan speed was 2° min^{-1}. Background counts of 10 s were taken at each end of the scan by the stationary-crystal–stationary-counter technique. The (011) reflection was monitored after every 50 measurements and showed good stability. An error $\sigma(I) = [(0{\cdot}02I)^2 + N_o + k^2N_b]^{\frac{1}{2}}$ was assigned to the net intensity $I = N_o - kN_b$ in order to establish the weights $w = 4F^2/\sigma^2(F^2)$ for subsequent least-squares refinement, where N_o is the gross count, N_b is the background count, k is the ratio of scan time to background time, and F^2 are the intensities corrected for Lorentz and polarization effects by the expression $L_p^{-1} = (2 \sin 2\theta)/(\cos^2 2\theta_m + \cos^2 2\theta)$ where $2\theta_m$ is the monochromator setting angle. The 139 reflections for which either $I < 0$ or $\sigma(I)/I > 0{\cdot}5$ were not used in the structure analysis. No absorption corrections were made.

Solution and Refinement of the Structure.—A scale factor and overall temperature factor were computed by Wilson's method and used to calculate a set of normalized structure factors. The structure was solved by reiterative application

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[6] ORTEP, a FORTRAN thermal ellipsoid plot program by C. K. Johnson, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

[7] A modified version of the Busing, Martin and Levy FORTRAN function and error program, OR-FFE, by J. Gvildys, Argonne National Laboratory Program Library B 115.

of Sayre's equation[8] to a set of 209 E values $\geq 1{\cdot}5$. The correct solution, which assumed positive signs for $(\bar{1},1,3)$, (0,2,3), (2,5,1), (1,3,0), and (1,13,0) and negative signs for $(\bar{1},5,3)$ and (3,1,7), gave a consistency index $C = \langle|E_{\mathbf{h}}\Sigma_{\mathbf{k}}E_{\mathbf{k}}E_{\mathbf{h-k}}|\rangle/\langle|E_{\mathbf{h}}|\Sigma_{\mathbf{k}}|E_{\mathbf{k}}||E_{\mathbf{h-k}}|\rangle = 0{\cdot}94$ after six cycles. The chlorine, oxygen, and carbon atoms were located in an E-map[8] based on the 209 signs, and a structure-factor calculation gave R 0·414 and the weighted value R' 0·629 $\{R' = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{\frac{1}{2}}\}$.

After three cycles of full-matrix least-squares refinement of positions and isotropic temperature factors, with a program described in ref. 9 (atomic scattering factors for chlorine, oxygen and carbon taken from ref. 10), R was 0·216 and R' 0·307. An analysis of R as a function of sin θ showed an increase from *ca.* 0·14 for the innermost reflections to 0·40 for the outermost. The most noticeable features of a difference-Fourier map calculated[11] at this stage were the large residuals in the vicinity of the chlorine atoms. However, after anisotropic temperature factors were introduced, by use of a program described in ref. 12, for the chlorine, oxygen, and carbon atoms, R was reduced to 0·084 and R' to 0·142 after two cycles of refinement. The hydrogen atoms (whose scattering factors were taken from ref. 13) were now readily identified in an electron-density difference map, with peak heights between 0·87 and 1·14 eÅ^{-3}. Five more cycles of full-matrix refinement, with anisotropic thermal parameters for chlorine, oxygen, and carbon, and isotropic parameters for hydrogen converged at R 0·056 and R' 0·087. The mean parameter shift in the final cycle was $<0{\cdot}01\sigma$, while the maximum shift was 0·09σ. A difference-Fourier map from which all atoms had been subtracted showed no peaks $>0{\cdot}33$ eÅ^{-3}. Atomic parameters and their standard deviations as calculated in the final least-squares cycle are listed in Table 5. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20293 (2 pp., 1 microfiche).*

TABLE 5

Final atom parameters (× 10^4) with estimated standard errors in parentheses

	x/a	y/b	z/c	β_{11} *	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl(6)	−2587(2)	4058(1)	4041(1)	441(4)	90(1)	166(1)	70(2)	12(2)	−12(1)
Cl(7)	−3379(2)	1098(1)	2309(1)	447(5)	139(1)	138(1)	10(2)	−114(2)	−27(1)
O	2005(4)	−348(2)	4189(2)	407(9)	76(2)	100(2)	38(4)	16(4)	6(2)
C(1)	954(6)	1517(3)	3271(3)	283(10)	76(3)	78(3)	5(4)	19(4)	6(2)
C(2)	1974(5)	726(3)	4203(3)	246(9)	78(3)	79(3)	24(4)	16(4)	1(2)
C(3)	2881(7)	1515(4)	5175(4)	342(12)	101(4)	95(3)	10(6)	−33(5)	2(3)
C(4)	1912(8)	2727(4)	4965(4)	360(13)	89(4)	128(4)	3(6)	−30(6)	−21(3)
C(5)	1350(6)	2816(3)	3669(3)	293(11)	77(3)	100(3)	−14(5)	21(5)	13(3)
C(6)	−1028(6)	3077(3)	3254(3)	339(12)	75(3)	94(3)	25(5)	0(5)	16(3)
C(7)	−1496(6)	1754(3)	3350(3)	274(10)	70(3)	80(3)	10(4)	−20(4)	3(2)

Hydrogen atom parameters (× 10^4) and isotropic temperature factors

				B/Å^2
H(1)	1309(72)	1298(36)	2357(38)	6·6(1·1)
H(3A)	4276(99)	1578(53)	5134(52)	9·0(1·6)
H(3B)	2500(71)	1083(39)	5947(36)	6·5(1·1)
H(4A)	2954(74)	3442(44)	5253(39)	7·0(1·1)
H(4B)	659(66)	2866(34)	5438(31)	4·7(0·9)
H(5)	2407(75)	3245(40)	3401(34)	5·8(1·0)
H(6)	−1172(77)	3346(46)	2466(42)	7·1(1·1)
H(7)	−1984(55)	1493(36)	4141(30)	4·4(0·8)

* Anisotropic temperature factors are in the form exp $[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

We thank Wendell Dilling for supplying the crystals and for his continuing interest in this problem.

[1/1618 *Received, 6th September,* 1971]

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

[8] D. Sayre, *Acta Cryst.*, 1952, **5**, 60; R. E. Long, ' A Program for Phase Determination by Reiterative Application of Sayre's Equation,' Ph.D. Thesis, University of California at Los Angeles, 1965.

[9] DOWLS, an isotropic least-squares refinement program for the 1130 computer by F. P. Boer and F. P. van Remoortere.

[10] ' International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, p. 201.

[11] Argonne National Laboratory Program Library, B 149, a version of Shoemaker, Sly, and Van der Hende's ERFR 2 by J. Gvildys.

[12] ANL FLS 14E, by J. Gvildys, a version of Busing, Martin, and Levy's OR FLS).

[13] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.* 1965 **42** 3175.