Crystal and Molecular Structure of ' Perpendicular ' 9,9-Dichloro-*trans*,-*trans*-bicyclo[6.1.0]non-4-ene Oxide

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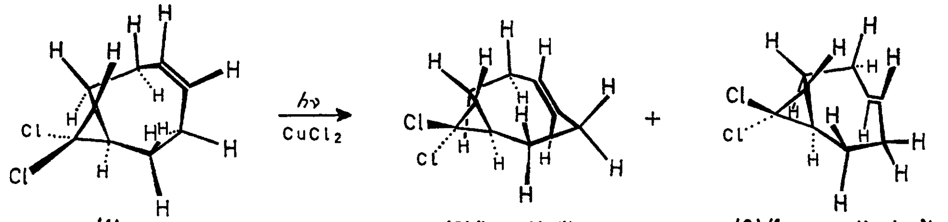
The crystal and molecular structure of the title compound has been determined by single-crystal *X*-ray diffraction techniques. Crystals are monoclinic space group $P2_1/n$, with unit cell dimensions a = 8·968(4), b = 8·835(4), c = 12·121(4) Å, β = 93·92(2)°, Z = 4. Diffractometer data were refined by full-matrix least-squares methods to R 0·040 for 1189 observed reflections. The dihedral angle between planes defined by the three-membered rings is 70·3°. The transannular distance between these rings, calculated from the midpoints of the two appropriate bonds, is 2·63 Å.

DURING a study of the spectral and chemical transannular interactions in eight-membered rings,[1] the *cis*-alkene (1) was photoisomerized to a mixture of two *trans*-conformers (2) and (3),[2] which were separable by preparative gas chromatography. Since the conformation of the predominant *trans*-product could not be determined by usual methods, and since this material is a liquid at ambient temperature, it was converted stereospecifically to its solid epoxide derivative,[1b] and an *X*-ray diffraction study was undertaken. The study showed that this epoxide, and hence the major olefin produced in the isomerization, has the ' perpendicular ' conformation.†



(1) (2) ('parallel') (3) ('perpendicular')

EXPERIMENTAL

Colourless crystals of 9,9-dichloro-*trans*,*trans*-bicyclo-[6.1.0]non-4-ene oxide were grown by slow evaporation from pentane. Preliminary unit-cell and space-group data were determined from Weissenberg photographs with Cu-K_α radiation (λ = 1·5418 Å); cell constants were computed by least-squares methods, from 15 reflections.

Crystal Data.—$C_9H_{12}Cl_2O$, M = 207·1. Monoclinic, a = 8·968(4), b = 8·835(4), c = 12·121(4) Å, β = 93·92(2)°, U = 958·1(3) Å^3, D_c = 1·436, Z = 4, D_m = 1·43, $F(000)$ = 464. Mo-K_α radiation λ = 0·7107 Å; μ(Mo-K_α) = 6·2 cm^{-1}, Space group $P2_1/n$.

Intensity data were collected on a Syntex $P\bar{1}$ automatic diffractometer. A θ—2θ scan at variable rate was employed. Four standard reflections were measured every 100 reflections, and were used to correct for a rather large (66%) decrease in intensity with time, due to crystal sublimation. The 1338 reflections with $I \geq 1{\cdot}2\sigma(I)$ were considered observed, and used in the analysis. The remaining 359 reflections were considered unobserved, and flagged with a minus sign.

Structure Determination and Refinement.—The positions of the two chlorine and three cyclopropyl-carbon atoms were deduced from a sharpened three-dimensional Patterson function. Two Fourier syntheses located all remaining non-hydrogen atoms, and one additional Fourier synthesis was used to refine these parameters. R was calculated to be 0·19, at this stage. After three cycles of full-matrix least-squares refinement with individual isotropic thermal parameters, R was reduced to 0·14. Three additional least-squares cycles with anisotropic thermal parameters for all non-hydrogen atoms reduced R to 0·069. All twelve hydrogen atoms were located by a difference-Fourier synthesis, and refined with isotropic thermal parameters. Two final least-squares cycles reduced R to 0·040, based on 1189 observed reflections.‡

Calculations were performed on an IBM 360/65 computer. The quantity minimized in the least-squares calculations was $\Sigma w(|F_o| - |F_c|)^2$. The following weighting scheme was employed: $\sqrt{w} = |F_o|/F_{low}$ if $|F_o| < F_{low}$, $= 1{\cdot}0$ if $F_{low} \leq |F_o| \leq F_{up}$, $= F_{up}/|F_o|$ if $|F_o| > F_{up}$ where $F_{low} = 10{\cdot}0$ and $F_{up} = 15{\cdot}0$. Scattering factors for carbon and hydrogen were taken from ref. 3*a*, for chlorine from ref. 3*b*, and for oxygen from ref. 3*c*.

The molecular conformation, thermal ellipsoids, and atomic numbering for the molecule are illustrated in

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† We use ' perpendicular ' to describe the orientation of the plane of the cyclopropyl ring with respect to the axis of the double bond in (3) [or the corresponding C(6)–C(7) bond in Figures 1 and 2].

‡ Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20554 (3 pp., 1 microfiche). 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. are sent as full size copies).

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TABLE 1

Final positional and thermal parameters ($\times 10^4$) [a] for non-hydrogen atoms

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl(1)	2041(1)	−40(1)	423(1)	148(1)	152(1)	82(1)	−63(2)	−32(1)	−6(2)
Cl(2)	846(1)	1710(1)	2184(1)	99(1)	139(1)	149(1)	−15(2)	77(2)	−11(2)
O	7800(2)	2979(3)	2836(2)	100(3)	249(5)	102(2)	−20(6)	−28(4)	−69(6)
C(1)	2476(3)	1169(3)	1552(3)	91(4)	100(4)	76(3)	−16(6)	23(5)	16(5)
C(2)	3699(3)	2301(4)	1503(3)	85(4)	95(4)	65(2)	−10(7)	−5(5)	18(6)
C(3)	3894(3)	913(3)	2239(2)	102(4)	86(4)	55(2)	25(7)	17(5)	1(5)
C(4)	4145(4)	1078(5)	3474(3)	156(5)	119(5)	61(3)	−10(9)	36(6)	25(6)
C(5)	5802(4)	1452(5)	3800(3)	171(6)	155(6)	60(3)	52(10)	−26(6)	4(7)
C(6)	6256(3)	2696(5)	3065(3)	101(4)	152(6)	72(3)	24(8)	−22(5)	−38(6)
C(7)	6756(3)	2364(5)	1987(3)	80(4)	181(6)	84(3)	−21(8)	10(5)	−47(8)
C(8)	6173(4)	3274(5)	1002(3)	119(5)	181(7)	70(3)	−82(9)	42(6)	8(8)
C(9)	4683(4)	2555(5)	560(3)	117(4)	168(6)	63(3)	−78(9)	−7(5)	59(7)

[a] Numbers in parentheses here, and in succeeding Tables, are estimated standard deviations. The anisotropic temperature factor is of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

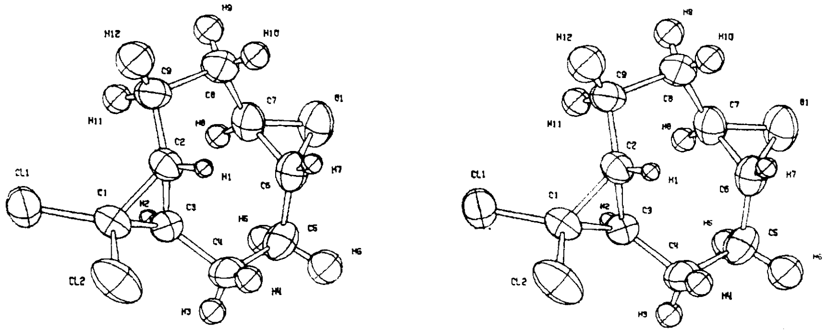

FIGURE 1 Stereoview of ' perpendicular ' 9,9-dichloro-*trans*,*trans*-bicyclo[6.1.0]non-4-ene oxide, showing the thermal ellipsoids (50% probability) and atomic numbering system used

TABLE 2

Final positional parameters ($\times 10^3$) and isotropic thermal parameters for hydrogen atoms

Atom	x	y	z	B/Å^2
H(1)	349(3)	317(3)	193(2)	0·9(0·5)
H(2)	445(3)	16(4)	196(2)	1·0(0·5)
H(3)	388(3)	17(4)	379(3)	2·2(0·6)
H(4)	357(4)	191(4)	371(3)	2·2(0·7)
H(5)	636(5)	61(5)	366(3)	3·3(0·9)
H(6)	590(5)	180(5)	463(4)	4·1(0·9)
H(7)	571(5)	366(6)	313(3)	1·4(1·1)
H(8)	697(4)	125(4)	183(3)	2·1(0·7)
H(9)	676(4)	330(4)	44(3)	2·8(0·8)
H(10)	600(4)	429(5)	127(3)	2·4(0·8)
H(11)	485(4)	156(5)	20(3)	2·6(0·8)
H(12)	416(5)	324(5)	2(4)	4·1(1·0)

TABLE 3

Intramolecular distances (Å)

(*a*) Bond distances

Cl(1)–C(1)	1·759(3)	C(8)–C(9)	1·542(5)
Cl(2)–C(1)	1·762(3)	C(2)–H(1)	0·95(3)
O–C(6)	1·452(4)	C(3)–H(2)	0·91(3)
O–C(7)	1·449(4)	C(4)–H(3)	0·93(3)
C(1)–C(2)	1·489(4)	C(4)–H(4)	0·95(3)
C(1)–C(3)	1·490(4)	C(5)–H(5)	0·92(4)
C(2)–C(3)	1·520(4)	C(5)–H(6)	1·05(4)
C(2)–C(9)	1·507(5)	C(6)–H(7)	0·99(5)
C(3)–C(4)	1·505(5)	C(7)–H(8)	1·02(4)
C(4)–C(5)	1·547(5)	C(8)–H(9)	0·89(4)
C(5)–C(6)	1·489(6)	C(8)–H(10)	0·96(4)
C(6)–C(7)	1·440(5)	C(9)–H(11)	1·00(4)
C(7)–C(8)	1·503(6)	C(9)–H(12)	0·99(4)

(*b*) Selected transannular distances

C(2)–C(6)	2·894(4)	C(3)–C(7)	2·904(5)
C(2)–C(7)	2·765(4)	H(1)–H(7)	2·42(5)
C(3)–C(6)	2·771(5)	H(2)–H(8)	2·48(5)

Figure 1.[4] Final positional and thermal parameters, with their estimated standard deviations, are given in Tables 1 and 2. Intramolecular distances and angles, with their

TABLE 4

Intramolecular angles (deg.)

C(6)–O–C(7)	59·5(2)	H(2)–C(3)–C(4)	113(2)
Cl(1)–C(1)–Cl(2)	110·9(2)	H(3)–C(4)–C(3)	108(2)
Cl(1)–C(1)–C(2)	120·1(2)	H(3)–C(4)–C(5)	111(2)
Cl(1)–C(1)–C(3)	118·6(2)	H(3)–C(4)–H(4)	112(3)
Cl(2)–C(1)–C(2)	118·1(2)	H(4)–C(4)–C(3)	109(2)
Cl(2)–C(1)–C(3)	120·0(2)	H(4)–C(4)–C(5)	107(2)
C(2)–C(1)–C(3)	61·4(2)	H(5)–C(5)–C(4)	108(3)
C(1)–C(2)–C(3)	59·3(2)	H(5)–C(5)–C(6)	108(3)
C(1)–C(2)–C(9)	127·0(3)	H(5)–C(5)–H(6)	114(4)
C(3)–C(2)–C(9)	121·0(3)	H(6)–C(5)–C(4)	109(2)
C(1)–C(3)–C(2)	59·3(2)	H(6)–C(5)–C(6)	110(2)
C(1)–C(3)–C(4)	127·2(3)	H(7)–C(6)–O	110(3)
C(2)–C(3)–C(4)	120·6(3)	H(7)–C(6)–C(5)	116(3)
C(3)–C(4)–C(5)	110·5(3)	H(7)–C(6)–C(7)	116(3)
C(4)–C(5)–C(6)	107·6(3)	H(8)–C(7)–O	112(2)
O–C(6)–C(5)	123·0(3)	H(8)–C(7)–C(6)	116(2)
O–C(6)–C(7)	60·1(2)	H(8)–C(7)–C(8)	115(2)
C(5)–C(6)–C(7)	120·5(3)	H(9)–C(8)–C(7)	116(2)
O–C(7)–C(6)	60·4(2)	H(9)–C(8)–C(9)	107(2)
O–C(7)–C(8)	122·5(3)	H(9)–C(8)–H(10)	110(3)
C(6)–C(7)–C(8)	119·9(3)	H(10)–C(8)–C(7)	107(2)
C(7)–C(8)–C(9)	107·6(3)	H(10)–C(8)–C(9)	110(2)
C(8)–C(9)–C(2)	109·6(3)	H(11)–C(9)–C(8)	111(2)
H(1)–C(2)–C(1)	110(2)	H(11)–C(9)–C(2)	108(2)
H(1)–C(2)–C(3)	110(2)	H(11)–C(9)–H(12)	110(3)
H(1)–C(2)–C(9)	116(2)	H(12)–C(9)–C(8)	110(3)
H(2)–C(3)–C(1)	112(2)	H(12)–C(9)–C(2)	108(3)
H(2)–C(3)–C(2)	115(2)		

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estimated standard deviations, appear in Tables 3 and 4, respectively.

DISCUSSION

The eight-membered ring of 'perpendicular' 9,9-dichloro-*trans,trans*-bicyclo[6.1.0]non-4-ene oxide exists in the 'twisted crown' conformation [5,6] (Figure 1).* Inspection of molecular models reveals that this conformation is preferred for two reasons: (i) it maximizes the distance between transannular hydrogen atoms H(1) and H(7), and H(2) and H(8), without causing excessive bond-angle deformation; and (ii) it staggers hydrogen atoms on the C(4)–C(5) and C(8)–C(9) bridges (Figure 2). Even in this conformation, the H(1)–H(7) and H(2)–H(8) distances (2·42 and 2·48 Å) are of the order of the sum of the van der Waals radii (2·4 Å) of the two hydrogen atoms. The marked effect of nonbonded hydrogen–hydrogen interactions on the conformation of medium rings is discussed in ref. 7.

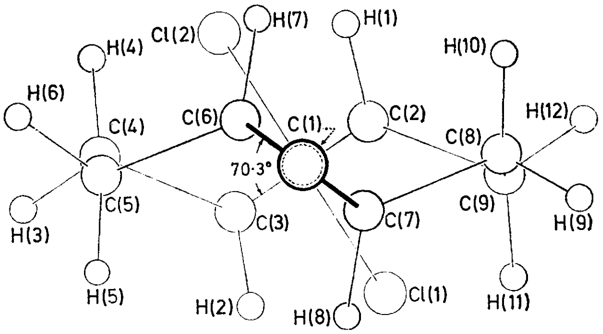

FIGURE 2 View down O–C(1), showing the 70·3° dihedral angle between the cyclopropyl [C(1)–C(2)–C(3)] and epoxide [O–C(6)–C(7)] planes, and the staggering of methylene hydrogen atoms. Atomic radii are not to scale

The dihedral angle between planes defined by the cyclopropyl and epoxide rings is 70·3°. Hendrickson [8] has calculated the corresponding dihedral angles (ϕ) for interconvertible cyclo-octane conformers having D_2 symmetry (*i.e.*, boat-crown), and has found the minimum energy conformer, also a twisted crown, to have $\phi = 72°$. The transannular distance between the mid-points of bonds C(2)–C(3) and C(6)–C(7) is 2·63 Å. The effective distance is expected to be shorter, as a result of bowing out of the Walsh orbitals [9] which constitute these bonds. Carbon–carbon bond distances in the C(4)–C(5) and C(8)–C(9) bridges (1·547 and 1·542 Å) compare favourably with the 'normal' carbon–carbon single-bond distance [1·537(5) Å].[10] Shortening of the four carbon–carbon bonds joining the three-membered rings (mean 1·501 Å) is consistent with their increased *s* character.[11]

The cyclopropyl ring is not equilateral,[12] probably as a consequence of the strain induced by ring fusion, although microwave studies of 1,1-dichlorocyclopropane have shown its three-membered ring to be nearly equilateral.[12] The long C(2)–C(3) bond (1·520 Å), relative to C(1)–C(2) and C(1)–C(3) (mean 1·490 Å), has been recently observed in a similar ring-fused 1,1-dichlorocyclopropane,[13] in which the mean C(1)–C(5) bond is 1·53 and not the reported 1·56 Å. The mean carbon–chlorine bond length (1·761 Å) is longer than that encountered in the parent 1,1-dichlorocyclopropane (1·734 Å).[12] Accordingly, the Cl–C(1)–Cl angle (110·9°) is smaller than that found in the parent compound (114·6°).[12] This difference may be attributed to van der Waals repulsion between the chlorine atoms and their proximate pseudoaxial cyclopropylcarbinyl hydrogen atoms, not present in 1,1-dichlorocyclopropane. Indeed, the Cl(1)–H(11) and Cl(2)–H(4) distances (2·919 and 2·962 Å, respectively) are of the order of the sum of the van der Waals radii for chlorine and hydrogen ($1·8 + 1·2 = 3·0$ Å).

The epoxide ring is equilateral, as has been reported for at least one other *trans*-fused epoxide.[14] The mean of the C(6)–O and C(7)–O bonds (1·451 Å) is comparable to that of the parent ethylene oxide (1·44 Å), determined from microwave studies.[15]

There was only one intermolecular contact less than the sum of the van der Waals radii: the Cl(2) · · · O distance of 3·105(3) Å is slightly smaller than the van der Waals separation for chlorine and oxygen (3·2 Å), but does not represent a significant intermolecular attraction.

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* The related *trans-syn-trans*-1,2,5,6-tetrabromocyclo-octane has also been found to exist in the twisted crown conformation.[6]

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