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(2*RS*,4*RS*)-*cis*-2-[*cis*-1-Chloro-4-(2-chloro-2-propyl)cyclohexyl]-4-(2-chloro-2-propyl)-1-cyclohexanone, $C_{18}H_{29}Cl_3O$

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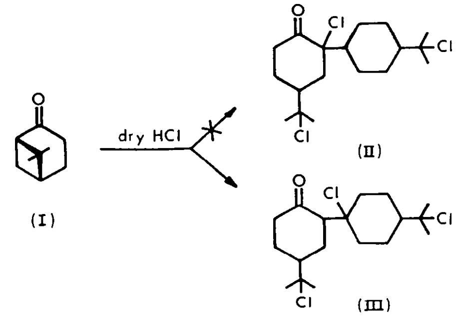
Abstract. $M_r = 367{\cdot}8$, triclinic, $P\bar{1}$, $a = 6{\cdot}403\,(1)$, $b = 10{\cdot}616\,(2)$, $c = 14{\cdot}500\,(2)$ Å, $\alpha = 94{\cdot}13\,(2)$, $\beta = 97{\cdot}85\,(2)$, $\gamma = 96{\cdot}86\,(2)°$, $V = 965{\cdot}5$ Å^3, $Z = 2$, $D_m = 1{\cdot}26\,(1)$, $D_x = 1{\cdot}265$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 4{\cdot}76$ cm^{-1}, $F(000) = 392$, $T = 293$ K, final $R = 0{\cdot}065$ for 1794 observed reflections. The two chloropropyl side chains are each disordered between two rotameric forms. The mean planes through the two cyclohexane chairs are inclined by 64·2 (4)° to one another, with a staggered conformation about the C(2)—C(1′) bond and the Cl substituent axial; all other substituents are equatorial.

Introduction. As part of a detailed study of the acid-catalysed ring opening of pinane derivatives we had occasion to re-examine the reaction of nopinone (I) with dry hydrogen chloride gas. The major product of this reaction was originally (Wallach & Blumann, 1907) assigned structure (II), and later (Lewis & Williams, 1968) reassigned as (III). In order to confirm the structure and determine relative stereochemistry a single-crystal X-ray structure determination was performed.



Experimental. Colourless crystal 0·51 × 0·16 × 0·10 mm, from ethanol, D_m by flotation (aqueous potassium iodide solution). Nicolet $R3m$ automated four-circle diffractometer, graphite-monochromated Mo $K\alpha$, lattice parameters from 23 reflections in range $30 < 2\theta < 32°$; space group $P\bar{1}$, $\theta/2\theta$ scans, $2\theta_{\max} = 48°$, standard reflections 200,021,013, max. intensity variation 28%; 3056 unique reflections measured, 1794 with $I > 3\sigma(I)$ used in refinement, range of hkl ±7, ±12, 0–16, no absorption correction; direct methods, blocked-cascade least-squares refinement on F, disordered C(9), C(9′), Cl(1) and Cl(3) refined with fixed C—C and C—Cl bond lengths (1·55 and 1·78 Å, respectively) and site-occupancy factors of $\frac{1}{2}$; all non-H atoms anisotropic except C(9) and C(9′) which had fixed isotropic thermal parameters, H atoms included in calculated positions with isotropic thermal parameters equal to isotropic equivalent of their carrier atoms (C—H 0·96 Å); 211 parameters refined, $R = 0{\cdot}065$, $wR = 0{\cdot}072$, $w = [\sigma^2(F) + 0{\cdot}0017F^2]^{-1}$, $S = 1{\cdot}65$, max. $(\Delta/\sigma) = 0{\cdot}013$ [C(3) z coordinate], av. $(\Delta/\sigma) = 0{\cdot}003$, $\Delta\rho = -0{\cdot}37$ to $+0{\cdot}40$ e Å^{-3}. All calculations on a Nova 4X computer using *SHELXTL* (Sheldrick, 1981), atomic scattering factors of *SHELXTL* used.

Discussion. Positional parameters and equivalent isotropic thermal parameters for the non-H atoms are listed in Table 1.† Bond lengths and angles are in Table 2. Fig. 1 shows a perspective view of the molecule and includes the atom labelling.

The study confirms the structure proposed by Lewis & Williams (1968) and establishes the relative stereochemistry as shown in Fig. 1. The two 2-chloro-2-propyl substituents are each disordered between two of the three possible staggered rotamers with 0·5 population factors. For each, the disordered carbon common to both rotamers, C(8) and C(8′), refined successfully as a single C atom. The two cyclohexane rings are chair conformers whose mean planes are inclined at 64·2 (4)° to one another and have a staggered conformation about the C(2)—C(1′) bond. Substituents are equatorial except for Cl(2), which is axial. The relatively long C(1′)—Cl(2) bond length [1·862 (4) Å] reflects the steric crowding at this centre and accounts for the ease with which the substrate loses HCl (Lewis & Williams, 1968).

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† Lists of structure amplitudes, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39244 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atom coordinates* (×10⁴) *and temperature factors* (Å² ×10³)

	x	y	z	$U_{\rm eq}$
Cl(2)	1656 (2)	573 (1)	−809 (1)	59 (1)*
O(1)	7012 (5)	4086 (3)	−571 (2)	54 (1)*
C(1)	6892 (7)	3332 (4)	9 (3)	38 (2)*
C(2)	5066 (6)	2253 (4)	−20 (3)	34 (2)*
C(3)	4051 (7)	2500 (4)	872 (3)	40 (2)*
C(4)	5617 (7)	2463 (4)	1754 (3)	38 (2)*
C(5)	7532 (7)	3491 (5)	1765 (3)	46 (2)*
C(6)	8517 (7)	3394 (5)	867 (3)	48 (2)*
C(7)	4638 (4)	2546 (2)	2664 (3)	44 (2)*
C(8)	6291 (8)	2355 (6)	3544 (3)	55 (2)*
C(9*A*)†	2938 (22)	1386 (12)	2691 (17)	40
C(9*B*)†	3561 (32)	3756 (12)	2841 (18)	40
Cl(1*A*)†	2368 (5)	1374 (4)	2563 (4)	72 (2)*
Cl(1*B*)†	3681 (9)	4041 (3)	2827 (6)	72 (1)*
C(1′)	3501 (7)	2023 (4)	−939 (3)	35 (2)*
C(2′)	4589 (7)	1683 (5)	−1773 (3)	43 (2)*
C(3′)	3123 (8)	1474 (5)	−2707 (3)	49 (2)*
C(4′)	1938 (7)	2639 (4)	−2871 (3)	42 (2)*
C(5′)	709 (7)	2873 (5)	−2064 (3)	42 (2)*
C(6′)	2141 (7)	3066 (4)	−1124 (3)	37 (2)*
C(7′)	634 (5)	2559 (3)	−3854 (3)	57 (2)*
C(8′)	2024 (9)	2463 (6)	−4659 (3)	69 (2)*
C(9′*A*)†	−498 (24)	3761 (11)	−3975 (16)	40
C(9′*B*)†	−1404 (15)	1579 (12)	−3971 (14)	40
Cl(3*A*)†	−598 (15)	3964 (6)	−3974 (6)	136 (2)*
Cl(3*B*)†	−1356 (6)	1209 (3)	−4046 (5)	96 (2)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

† Disordered. Population factor 0·5.

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

Cl(2)—C(1′)	1·862 (4)	O(1)—C(1)	1·205 (6)
C(1)—C(2)	1·530 (6)	C(1)—C(6)	1·501 (6)
C(2)—C(3)	1·545 (6)	C(2)—C(1′)	1·539 (6)
C(3)—C(4)	1·519 (6)	C(4)—C(5)	1·539 (6)
C(4)—C(7)	1·537 (6)	C(5)—C(6)	1·524 (7)
C(7)—C(8)	1·584 (6)	C(7)—C(9*A*)	1·550 (14)
C(7)—C(9*B*)	1·550 (17)	C(7)—Cl(1*A*)	1·780 (5)
C(7)—Cl(1*B*)	1·780 (5)	C(1′)—C(2′)	1·518 (7)
C(1′)—C(6′)	1·505 (6)	C(2′)—C(3′)	1·525 (6)
C(3′)—C(4′)	1·542 (7)	C(4′)—C(5′)	1·519 (7)
C(4′)—C(7′)	1·541 (6)	C(5′)—C(6′)	1·520 (6)
C(7′)—C(8′)	1·567 (7)	C(7′)—C(9′*A*)	1·550 (14)
C(7′)—C(9′*B*)	1·550 (10)	C(7′)—Cl(3*A*)	1·777 (8)
C(7′)—Cl(3*B*)	1·779 (4)		

O(1)—C(1)—C(2)	124·7 (4)	O(1)—C(1)—C(6)	122·6 (4)
C(2)—C(1)—C(6)	112·7 (4)	C(1)—C(2)—C(3)	106·3 (3)
C(1)—C(2)—C(1′)	115·4 (4)	C(3)—C(2)—C(1′)	115·4 (3)
C(2)—C(3)—C(4)	111·9 (4)	C(3)—C(4)—C(5)	109·1 (4)
C(3)—C(4)—C(7)	114·4 (4)	C(5)—C(4)—C(7)	112·5 (3)
C(4)—C(5)—C(6)	112·4 (4)	C(1)—C(6)—C(5)	112·3 (4)
C(4)—C(7)—C(8)	111·9 (3)	C(4)—C(7)—C(9*A*)	111·2 (9)
C(4)—C(7)—Cl(1*A*)	109·2 (3)	C(4)—C(7)—C(9*B*)	115·1 (10)
C(4)—C(7)—Cl(1*B*)	110·1 (4)	Cl(2)—C(1′)—C(2)	105·3 (3)
Cl(2)—C(1′)—C(2′)	105·6 (3)	C(2)—C(1′)—C(2′)	112·2 (3)
Cl(2)—C(1′)—C(6′)	106·5 (3)	C(2)—C(1′)—C(6′)	114·9 (3)
C(2′)—C(1′)—C(6′)	111·5 (4)	C(1′)—C(2′)—C(3′)	114·5 (4)
C(2′)—C(3′)—C(4′)	110·5 (4)	C(3′)—C(4′)—C(5′)	108·9 (4)
C(3′)—C(4′)—C(7′)	113·1 (3)	C(5′)—C(4′)—C(7′)	115·3 (4)
C(4′)—C(5′)—C(6′)	112·2 (4)	C(1′)—C(6′)—C(5′)	114·5 (4)
C(4′)—C(7′)—C(8′)	113·2 (3)	C(4′)—C(7′)—C(9′*A*)	110·5 (8)
C(4′)—C(7′)—Cl(3*A*)	109·2 (4)	C(4′)—C(7′)—C(9′*B*)	112·7 (8)
C(4′)—C(7′)—Cl(3*B*)	111·3 (4)		

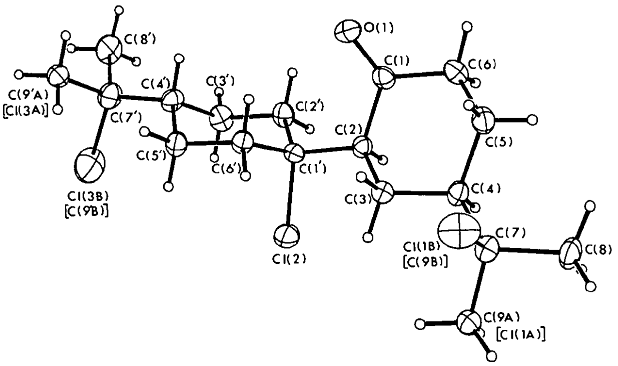
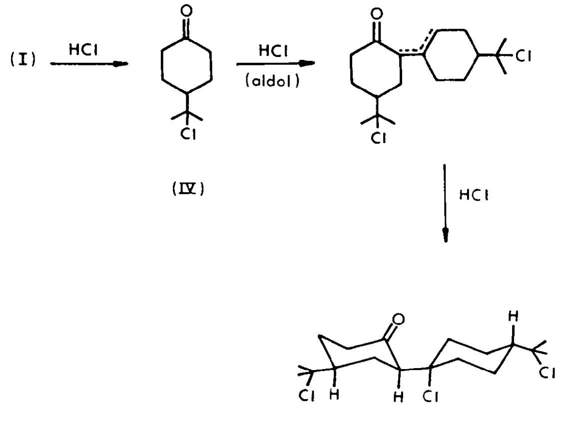


Fig. 1. Perspective view and atom labelling of the title compound. Thermal ellipsoids are drawn at the 30% probability level; H atoms with 0·10 Å radii.

The racemic nature of (III) obtained from optically pure (+)-nopinone (I) suggests the reaction involves the intermediacy of achiral 4-(2-chloro-2-propyl)-1-cyclohexanone (IV) which subsequently undergoes an intermolecular aldol condensation and stereospecific addition of HCl. This is supported by the isolation of (IV) from the reaction mixture and its conversion with HCl to (III).



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