

## 4,4-Dichlorotricyclo[5.4.0.0<sup>3,5</sup>]undeca-7,9,11-triene

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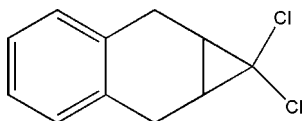
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Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å;  $R$  factor = 0.040;  $wR$  factor = 0.101; data-to-parameter ratio = 15.0.

The title compound,  $\text{C}_{11}\text{H}_{10}\text{Cl}_2$ , is a useful intermediate for the synthesis of 1*H*-cyclopropa[*b*]naphthalene. Strain in the molecule is evidenced by the fact that the cyclohexane ring is essentially planar and nearly coplanar with the benzene ring [dihedral angle 1.87 (18)°], and the cyclopropyl ring is almost perpendicular to the cyclohexane ring [dihedral angle 70.99 (12)°]. The molecules are loosely connected into one-dimensional chains by intermolecular  $\text{Cl}\cdots\text{Cl}$  interactions with a distance of 3.571 (1) Å. The centroid-to-centroid distance between stacked benzene rings is *ca* 5.89 Å, indicating that no  $\pi$ - $\pi$  stacking exists in the crystal structure.

### Related literature

For related literature, see: Browne *et al.* (1974); Halton (2003).



### Experimental

#### Crystal data

$\text{C}_{11}\text{H}_{10}\text{Cl}_2$	$V = 993.5$ (3) Å <sup>3</sup>
$M_r = 213.09$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 11.598$ (2) Å	$\mu = 0.60$ mm <sup>-1</sup>
$b = 5.8920$ (12) Å	$T = 298$ (2) K
$c = 14.861$ (3) Å	$0.26 \times 0.21 \times 0.18$ mm
$\beta = 101.97$ (3)°	

#### Data collection

Bruker SMART 1K CCD area-detector diffractometer	7291 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2002)	1765 independent reflections
$T_{\min} = 0.860$ , $T_{\max} = 0.900$	1363 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.036$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.040$	118 parameters
$wR(F^2) = 0.101$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.20$ e Å <sup>-3</sup>
1765 reflections	$\Delta\rho_{\text{min}} = -0.29$ e Å <sup>-3</sup>

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL and publCIF (Westrip, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2197).

### References

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**supplementary materials**

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### Comment

The title compound, (I), is a useful intermediate for the synthesis of 1*H*-cyclopropa[*b*]naphthalene, which is a highly strained but readily accessible molecule that has been used as a building block in organic synthesis. It can undergo a variety of reactions because relief of ring strain provides a potent thermodynamic driving force for the reactions (Halton, 2003). Strain in (I) is evidenced by the fact that the cyclohexane ring is essentially planar (Fig. 1) and nearly coplanar with the benzene ring with a dihedral angle of 1.87 (18)° and that the cyclopropyl ring is almost perpendicular to cyclohexane ring with a dihedral angle of 70.99 (12)°. The molecules pack to form one-dimensional chains connected by intermolecular Cl⋯Cl interactions with distance of 3.571 (1) Å (Fig. 2). The centroid to centroid distance between stacked benzene rings is *ca* 5.89 Å, which is very long indicating that no  $\pi$ - $\pi$  stacking exists in the crystal.

### Experimental

Following the general procedure of Browne *et al.* (1974) a mixture of 1,4-dihydronaphthalene (15g, 0.115 mol), 7 ml of diethylene glycol dimethyl, and 10 ml of tetrachloroethylene was stirred magnetically and brought to 115°C, and sodium trichloroacetate (25 g, 0.144 mol) was added in 1 g portions over a period of 1 h. The mixture was stirred and maintained near boiling (115–120°C) during the addition and for an additional half hour. After separating, washing, and drying the organic phase, concentration in vacuum afforded a brown oil which was distilled to give 7,7-dichlorobenzobicyclo[4.1.0]hept-3-ene (6.85 g, 47% based on the dihydronaphthalene used) and the single crystals were obtained by evaporation of a petroleum ether solution. b.p. 389–391 K at 1 mm, m.p. 328–330 K. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.03–2.05 (m, 2H); 2.76–2.82 (m, 2H), 3.18–3.25 (m, 2H), 7.10 (s, 4H).

### Refinement

H atoms were positioned geometrically and treated as riding, with C—H bond lengths constrained to 0.93 (aromatic CH), 0.97 Å (methylene CH<sub>2</sub>) and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$  (carrier aromatic C and methylene C).

### Figures

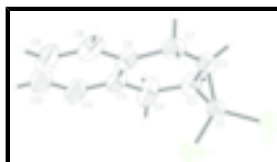


Fig. 1. The molecular structure of (I), with displacement ellipsoids drawn at the 40% probability level. H atoms are shown as spheres of arbitrary radius.



Fig. 2. Partial packing view of (I) showing Cl...Cl interaction. H atoms have been omitted for clarity.

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### Crystal data

$C_{11}H_{10}Cl_2$

$M_r = 213.09$

Monoclinic,  $P2_1/n$

Hall symbol:  $-P\ 2yn$

$a = 11.598\ (2)\ \text{\AA}$

$b = 5.8920\ (12)\ \text{\AA}$

$c = 14.861\ (3)\ \text{\AA}$

$\beta = 101.97\ (3)^\circ$

$V = 993.5\ (3)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 440$

$D_x = 1.425\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 6708 reflections

$\theta = 3.0\text{--}27.5^\circ$

$\mu = 0.60\ \text{mm}^{-1}$

$T = 298\ (2)\ \text{K}$

Chunk, colourless

$0.26 \times 0.21 \times 0.18\ \text{mm}$

### Data collection

Bruker SMART 1K CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298\ (2)\ \text{K}$

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2002)

$T_{\min} = 0.860$ ,  $T_{\max} = 0.900$

7291 measured reflections

1765 independent reflections

1363 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.036$

$\theta_{\text{max}} = 25.1^\circ$

$\theta_{\text{min}} = 3.6^\circ$

$h = -13 \rightarrow 13$

$k = -7 \rightarrow 6$

$l = -17 \rightarrow 17$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.101$

$S = 1.08$

1765 reflections

118 parameters

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0595P)^2 + 0.3188P]$$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.20\ \text{e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.29\ \text{e \AA}^{-3}$

Primary atom site location: structure-invariant direct methods Extinction correction: none

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) etc. and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.21220 (6)	1.03963 (10)	0.93462 (4)	0.0652 (2)
C12	0.23062 (6)	0.60334 (11)	1.02480 (4)	0.0674 (2)
C1	0.1572 (2)	0.7642 (4)	0.92994 (14)	0.0491 (5)
C2	0.1202 (2)	0.6470 (4)	0.84012 (15)	0.0554 (6)
H2	0.1358	0.4834	0.8414	0.066*
C3	0.0301 (2)	0.7219 (5)	0.89436 (15)	0.0614 (6)
H3	-0.0032	0.5987	0.9253	0.074*
C4	-0.0539 (2)	0.9095 (6)	0.86004 (18)	0.0837 (10)
H4A	-0.0484	1.0214	0.9086	0.100*
H4B	-0.1332	0.8481	0.8486	0.100*
C5	-0.0371 (2)	1.0298 (4)	0.77408 (14)	0.0574 (6)
C6	0.0445 (2)	0.9597 (4)	0.72401 (14)	0.0515 (6)
C7	0.1263 (2)	0.7628 (4)	0.75120 (15)	0.0596 (6)
H7A	0.2064	0.8157	0.7551	0.072*
H7B	0.1101	0.6507	0.7024	0.072*
C8	0.0505 (2)	1.0778 (5)	0.64359 (16)	0.0687 (7)
H8	0.1043	1.0319	0.6088	0.082*
C9	-0.0210 (3)	1.2590 (6)	0.61490 (19)	0.0821 (9)
H9	-0.0157	1.3343	0.5609	0.099*
C10	-0.1007 (3)	1.3307 (6)	0.6654 (2)	0.0828 (9)
H10	-0.1490	1.4551	0.6464	0.099*
C11	-0.1080 (2)	1.2166 (5)	0.74404 (17)	0.0727 (8)
H11	-0.1619	1.2651	0.7784	0.087*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C11	0.0862 (5)	0.0485 (4)	0.0576 (4)	-0.0129 (3)	0.0072 (3)	-0.0011 (3)
C12	0.0776 (5)	0.0628 (4)	0.0593 (4)	0.0120 (3)	0.0079 (3)	0.0130 (3)
C1	0.0556 (14)	0.0420 (12)	0.0501 (12)	0.0008 (10)	0.0114 (10)	0.0030 (10)
C2	0.0623 (15)	0.0446 (12)	0.0582 (13)	-0.0039 (11)	0.0103 (11)	-0.0032 (11)

## supplementary materials

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C3	0.0523 (15)	0.0740 (17)	0.0590 (13)	-0.0081 (12)	0.0144 (11)	0.0151 (13)
C4	0.0592 (17)	0.133 (3)	0.0629 (15)	0.0237 (17)	0.0224 (13)	0.0273 (17)
C5	0.0473 (14)	0.0767 (17)	0.0449 (12)	0.0016 (12)	0.0018 (10)	0.0006 (12)
C6	0.0462 (13)	0.0645 (15)	0.0408 (11)	-0.0113 (11)	0.0024 (9)	-0.0034 (11)
C7	0.0610 (16)	0.0676 (16)	0.0516 (13)	0.0007 (12)	0.0146 (11)	-0.0096 (12)
C8	0.0583 (16)	0.099 (2)	0.0470 (13)	-0.0164 (15)	0.0058 (11)	0.0071 (14)
C9	0.073 (2)	0.101 (2)	0.0627 (16)	-0.0193 (18)	-0.0080 (15)	0.0304 (16)
C10	0.071 (2)	0.085 (2)	0.0794 (19)	0.0047 (16)	-0.0157 (16)	0.0134 (17)
C11	0.0582 (16)	0.093 (2)	0.0596 (15)	0.0126 (15)	-0.0040 (12)	-0.0030 (15)

### *Geometric parameters (Å, °)*

C11—C1	1.740 (2)	C5—C11	1.391 (4)
C12—C1	1.764 (2)	C6—C8	1.397 (3)
C1—C3	1.481 (3)	C6—C7	1.500 (3)
C1—C2	1.485 (3)	C7—H7A	0.9700
C2—C7	1.502 (3)	C7—H7B	0.9700
C2—C3	1.512 (3)	C8—C9	1.365 (4)
C2—H2	0.9800	C8—H8	0.9300
C3—C4	1.491 (4)	C9—C10	1.372 (4)
C3—H3	0.9800	C9—H9	0.9300
C4—C5	1.508 (3)	C10—C11	1.366 (4)
C4—H4A	0.9700	C10—H10	0.9300
C4—H4B	0.9700	C11—H11	0.9300
C5—C6	1.383 (3)		
C3—C1—C2	61.31 (16)	C6—C5—C11	119.3 (2)
C3—C1—C11	120.06 (18)	C6—C5—C4	122.6 (2)
C2—C1—C11	120.33 (15)	C11—C5—C4	118.2 (2)
C3—C1—C12	118.33 (16)	C5—C6—C8	118.2 (2)
C2—C1—C12	118.03 (16)	C5—C6—C7	123.4 (2)
C11—C1—C12	110.92 (12)	C8—C6—C7	118.4 (2)
C1—C2—C7	121.5 (2)	C6—C7—C2	116.50 (19)
C1—C2—C3	59.20 (15)	C6—C7—H7A	108.2
C7—C2—C3	120.0 (2)	C2—C7—H7A	108.2
C1—C2—H2	115.0	C6—C7—H7B	108.2
C7—C2—H2	115.0	C2—C7—H7B	108.2
C3—C2—H2	115.0	H7A—C7—H7B	107.3
C1—C3—C4	121.9 (2)	C9—C8—C6	121.5 (3)
C1—C3—C2	59.49 (15)	C9—C8—H8	119.3
C4—C3—C2	120.6 (2)	C6—C8—H8	119.3
C1—C3—H3	114.6	C8—C9—C10	120.3 (3)
C4—C3—H3	114.6	C8—C9—H9	119.9
C2—C3—H3	114.6	C10—C9—H9	119.9
C3—C4—C5	116.6 (2)	C11—C10—C9	119.0 (3)
C3—C4—H4A	108.1	C11—C10—H10	120.5
C5—C4—H4A	108.1	C9—C10—H10	120.5
C3—C4—H4B	108.1	C10—C11—C5	121.8 (3)
C5—C4—H4B	108.1	C10—C11—H11	119.1
H4A—C4—H4B	107.3	C5—C11—H11	119.1

C3—C1—C2—C7	108.5 (3)	C3—C4—C5—C11	-175.2 (2)
C11—C1—C2—C7	-1.4 (3)	C11—C5—C6—C8	-1.3 (3)
C12—C1—C2—C7	-142.7 (2)	C4—C5—C6—C8	177.8 (2)
C11—C1—C2—C3	-110.0 (2)	C11—C5—C6—C7	179.1 (2)
C12—C1—C2—C3	108.8 (2)	C4—C5—C6—C7	-1.8 (4)
C2—C1—C3—C4	-109.2 (2)	C5—C6—C7—C2	-2.9 (3)
C11—C1—C3—C4	1.2 (3)	C8—C6—C7—C2	177.6 (2)
C12—C1—C3—C4	142.6 (2)	C1—C2—C7—C6	-66.7 (3)
C11—C1—C3—C2	110.39 (19)	C3—C2—C7—C6	3.4 (3)
C12—C1—C3—C2	-108.28 (19)	C5—C6—C8—C9	0.6 (4)
C7—C2—C3—C1	-111.0 (2)	C7—C6—C8—C9	-179.8 (2)
C1—C2—C3—C4	111.4 (3)	C6—C8—C9—C10	0.4 (4)
C7—C2—C3—C4	0.4 (4)	C8—C9—C10—C11	-0.7 (4)
C1—C3—C4—C5	66.1 (3)	C9—C10—C11—C5	-0.1 (4)
C2—C3—C4—C5	-4.8 (4)	C6—C5—C11—C10	1.1 (4)
C3—C4—C5—C6	5.6 (4)	C4—C5—C11—C10	-178.1 (3)

Fig. 1

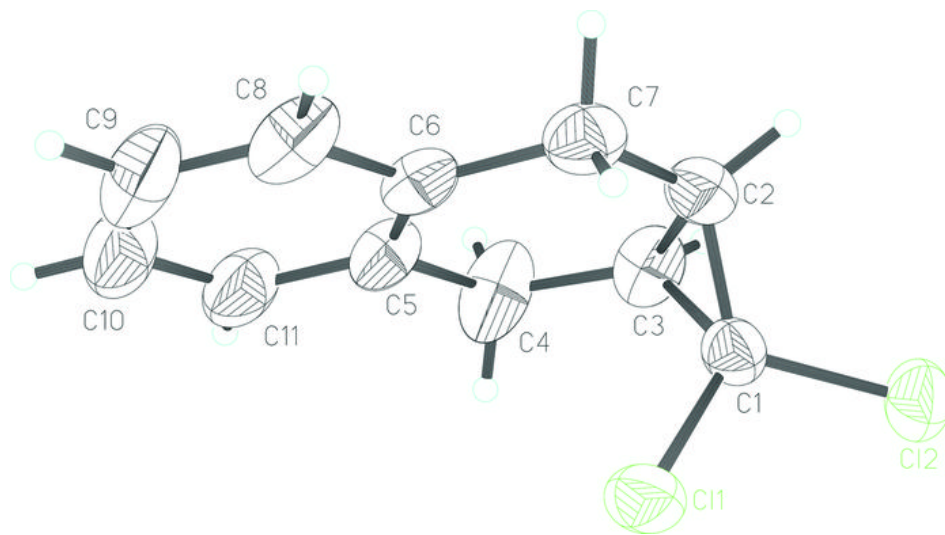




Fig. 2

