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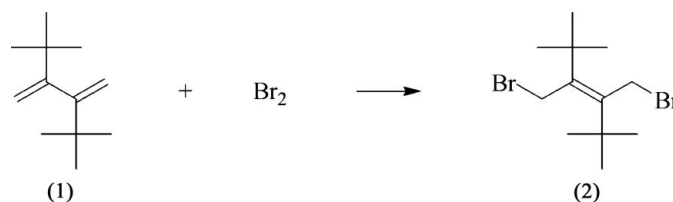
## Key indicators

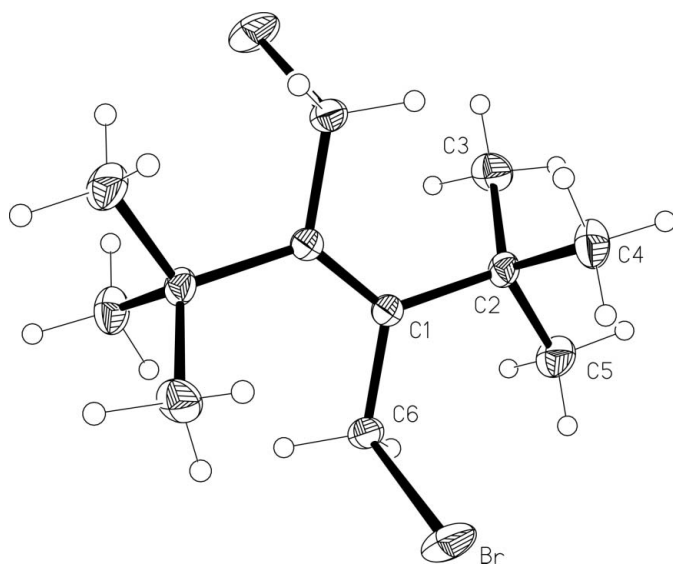
Single-crystal X-ray study  
 $T = 173$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å  
 $R$  factor = 0.027  
 $wR$  factor = 0.068  
Data-to-parameter ratio = 21.2For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.A sterically crowded molecule: (*E*)-3,4-bis(bromo-  
methyl)-2,2,5,5-tetramethylhex-3-eneThe title compound,  $\text{C}_{12}\text{H}_{22}\text{Br}_2$ , displays crystallographic  
inversion symmetry. Bond lengths  $\text{C}=\text{C} = 1.352$  (4) Å and  
 $\text{Csp}^2-\text{Csp}^3 = 1.574$  (3) Å are interpreted as symptoms of  
steric overcrowding. Molecules are linked into chains parallel  
to [101] by  $\text{Br}\cdots\text{Br}$  interactions of 3.4275 (9) Å.

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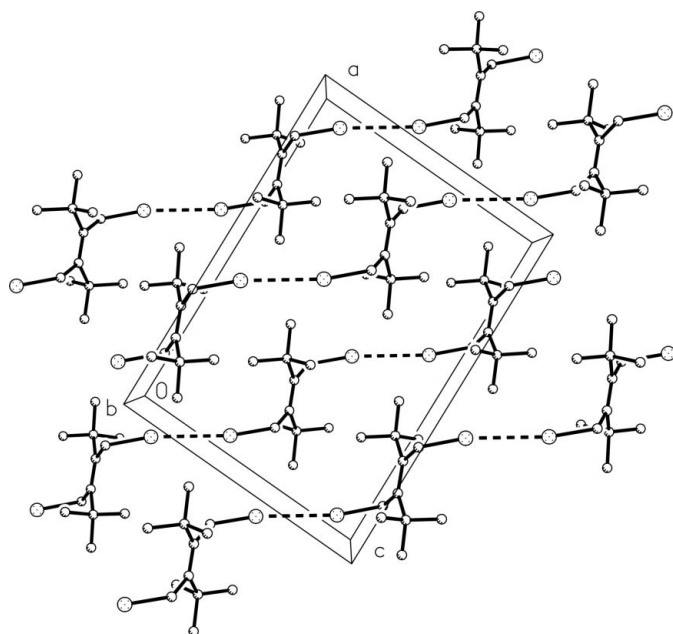
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## Comment

The highly hindered diene 3,4-bismethylene-2,2,5,5-tetra-  
methylhexane, (1), on treatment with bromine (in carbon  
tetrachloride at 273 K), provides predominantly the 1,4-addi-  
tion product (*E*)-3,4-bis(bromomethyl)-2,2,5,5-tetramethyl-  
hex-3-ene, (2) (Backer, 1939). During our studies of highly  
hindered oligoenes (Hänel, 1996; Hopf *et al.*, 2001), we have  
repeated this experiment and obtained single crystals of (2)  
suitable for X-ray structural analysis.The molecule of (2), which displays crystallographic inver-  
sion symmetry, is shown in Fig. 1. Because of this symmetry,  
IUPAC numbering cannot be used. Both the double bond  
 $\text{C1}=\text{C1}^i$  and the single bond  $\text{C1}-\text{C2}$  (symmetry code as in  
Table 1) may be regarded as significantly lengthened with  
respect to, for example, standard values of 1.331 Å for the  
central bond of the group  $(\text{C}-)_2\text{C}=\text{C}(\text{-C})_2$  and 1.522 Å for  
the central bond of  $(\text{C}-)_3\text{C}-\text{C}=\text{C}$  (Allen *et al.*, 1987). The  
single bonds of the butyl group, in contrast, display normal  
lengths. The angle  $\text{C1}^i-\text{C1}-\text{C2}$  is widened from the ideal  
 $120^\circ$  by *ca*  $6^\circ$ , at the expense of  $\text{C6}-\text{C1}-\text{C2}$ . These distor-  
tions may reasonably be attributed to steric pressure in the  
crowded system. Further evidence for this is provided by short  
intramolecular contacts  $\text{H3A}\cdots\text{H6B}^i$  1.89 and  $\text{H4B}\cdots\text{H6B}^i$   
1.94 Å. The geometry at the double bond is essentially planar,  
with a maximum torsion angle of  $-1.7$  (4) $^\circ$  about  $\text{C1}-\text{C1}^i$ .  
The configuration of the  $\text{CH}_2\text{Br}$  side chain is defined by the  
torsion angle  $\text{C2}-\text{C1}-\text{C6}-\text{Br} = 78.2$  (2) $^\circ$ .The most striking feature of the crystal packing is the  
formation of zigzag chains of molecules, with overall direction  
parallel to [101], via  $\text{Br}\cdots\text{Br}$  contacts of 3.4275 (9) Å (Fig. 2),  
symmetry operator  $(1-x, y, \frac{3}{2}-z)$ . The  $\text{C}-\text{Br}\cdots\text{Br}$  angles  
are equal by symmetry at 168.74 (6) $^\circ$ . This corresponds to a



**Figure 1**  
A view of the title compound, with displacement ellipsoids drawn at the 50% probability level. [Symmetry code for unlabelled atoms:  $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$ .



**Figure 2**  
A packing diagram of the title compound, viewed parallel to the *b* axis. Br...Br contacts are indicated by dashed lines. H atoms have been omitted.

type I interaction according to the classification of Pedireddi *et al.* (1994).

## Experimental

The diene, (1), was treated with bromine, as described by Backer (1939). The analytically pure adduct, (2), was obtained by preparative gas chromatography and characterized by NMR and MS analysis:  $^1\text{H}$  NMR (20 MHz,  $\text{CDCl}_3$ , internal standard TMS,  $\delta$ , p.p.m.): = 1.11 (s, 18H, *tert*-Bu), 4.1–4.9 (unresolved AB-*q*, 4H,  $\text{CH}_2$ ). Single crystals were obtained by slow evaporation of a solution in petroleum ether (b.p. 333 K).

## Crystal data

$\text{C}_{12}\text{H}_{22}\text{Br}_2$   
 $M_r = 326.12$   
Monoclinic,  $C2/c$   
 $a = 15.658$  (4) Å  
 $b = 7.3521$  (12) Å  
 $c = 11.284$  (2) Å  
 $\beta = 93.53$  (2)°  
 $V = 1296.6$  (5) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.671$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 60 reflections  
 $\theta = 10$ – $11.5^\circ$   
 $\mu = 6.22$  mm<sup>-1</sup>  
 $T = 173$  (2) K  
Block, colourless  
0.5 × 0.4 × 0.4 mm

## Data collection

Stoe STADI4 diffractometer  
 $\omega/\theta$  scans  
Absorption correction:  $\psi$  scan  
(*XEMP*; Siemens, 1994)  
 $T_{\min} = 0.035$ ,  $T_{\max} = 0.083$   
2458 measured reflections  
1487 independent reflections  
1341 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.035$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -20 \rightarrow 20$   
 $k = -9 \rightarrow 4$   
 $l = 0 \rightarrow 14$   
3 standard reflections  
frequency: 60 min  
intensity decay: none

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.027$   
 $wR(F^2) = 0.068$   
 $S = 1.10$   
1487 reflections  
70 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0302P)^2 + 1.7902P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.60$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.57$  e Å<sup>-3</sup>  
Extinction correction: *SHELXL97*  
(Sheldrick, 1997)  
Extinction coefficient: 0.0023 (4)

**Table 1**

Selected geometric parameters (Å, °).

Br—C6	1.989 (2)	C2—C4	1.536 (3)
C1—C1 <sup>i</sup>	1.352 (4)	C2—C3	1.540 (3)
C1—C6	1.495 (3)	C2—C5	1.546 (3)
C1—C2	1.574 (3)		
C1 <sup>i</sup> —C1—C6	120.0 (2)	C6—C1—C2	113.99 (17)
C1 <sup>i</sup> —C1—C2	126.0 (2)		
C2—C1—C6—Br	78.20 (19)	C6—C1—C1 <sup>i</sup> —C2 <sup>i</sup>	-1.7 (4)

Symmetry code: (i)  $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$ .

Methyl H atoms were located in difference syntheses, idealized ( $\text{C—H} = 0.98$  Å and  $\text{H—C—H} = 109.5^\circ$ ) and refined on the basis of rigid groups allowed to rotate but not tip. Methylene H atoms were placed in calculated positions ( $\text{C—H} = 0.99$  Å) and allowed to ride on their parent C atom.  $U_{\text{iso}}(\text{H})$  values were fixed at  $1.2U_{\text{eq}}$  of the parent atom.

Data collection: *DIF4* (Stoe & Cie, 1992); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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