$S = 1.031$
2544 reflections
220 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2 + 0.15P]$
where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none
Scattering factors from
International Tables for Crystallography (Vol. C)

Zsolnai, L. (1996). *XPMA. Molecular Geometry Program for a Silicon Graphics Computer.* University of Heidelberg, Germany.
Zsolnai, L. & Pritzkow, H. (1995). *ORTEP Program for a Silicon Graphics Computer.* University of Heidelberg, Germany.

Table 1. *Selected geometric parameters (Å, °)*

O1—C1'	1.383 (2)	C6—C1	1.399 (2)
O1—C2	1.390 (2)	C1—C7	1.496 (2)
O2—C7	1.318 (2)	C1'—C6'	1.386 (2)
O3—C7	1.210 (2)	C1'—C2'	1.399 (2)
O4—C9	1.442 (2)	C6'—C5'	1.387 (2)
C2—C3	1.390 (2)	C5'—C4'	1.376 (3)
C2—C1	1.395 (2)	C4'—C3'	1.383 (3)
C3—C4	1.378 (2)	C3'—C2'	1.392 (2)
C4—C5	1.377 (3)	C2'—C8	1.504 (2)
C5—C6	1.385 (3)	C8—C9	1.508 (2)
C1'—O1—C2	118.39 (11)	O2—C7—C1	112.70 (12)
O1—C2—C3	117.63 (15)	O1—C1'—C6'	123.27 (13)
O1—C2—C1	121.38 (13)	O1—C1'—C2'	115.23 (13)
C3—C2—C1	120.90 (14)	C6'—C1'—C2'	121.50 (14)
C4—C3—C2	120.2 (2)	C1'—C6'—C5'	119.6 (2)
C5—C4—C3	120.2 (2)	C4'—C5'—C6'	120.3 (2)
C4—C5—C6	119.7 (2)	C5'—C4'—C3'	119.5 (2)
C5—C6—C1	121.6 (2)	C4'—C3'—C2'	122.2 (2)
C2—C1—C6	117.49 (14)	C3'—C2'—C1'	116.99 (15)
C2—C1—C7	122.79 (13)	C3'—C2'—C8	121.12 (14)
C6—C1—C7	119.72 (14)	C1'—C2'—C8	121.89 (13)
O3—C7—O2	122.27 (14)	C2'—C8—C9	113.82 (14)
O3—C7—C1	125.03 (14)	O4—C9—C8	111.13 (14)

In the final refinement cycles, the reflections from the outermost resolution shell, 0.78–0.75 Å, were omitted on account of their weakness and poor agreement.

Data collection: Stoe IPDS software package. Cell refinement: Stoe IPDS software package. Data reduction: Stoe IPDS software package. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Zsolnai & Pritzkow, 1995) and *XPMA* (Zsolnai, 1996). Software used to prepare material for publication: *SHELXL93* and *ORTEP*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1191). Services for accessing these data are described at the back of the journal.

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Octamethylcuneane and Octamethyl-cubane: the First X-ray Crystal Structure of a Cuneane

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Abstract

In the crystal of octamethylcuneane (1,2,3,4,5,6,7,8-octa-methylpentacyclo[$3.3.0.0^{2,4}.0^{3,7}.0^{6,8}$]octane), $C_{16}H_{24}$, there are two independent molecules in the asymmetric unit. Octamethylcubane (1,2,3,4,5,6,7,8-octamethylpenta-cyclo[$4.2.0.0^{2,5}.0^{3,8}.0^{4,7}$]octane), $C_{16}H_{24}$, exhibits crystallographic $3m$ symmetry. Due to the eclipsed orientation of the methyl groups in octamethylcubane, the average bond length is extended to 1.563 (3) Å compared with cubane itself. In the cuneane derivative, the cage bond lengths vary between 1.517 (2) and 1.573 (2) Å in accordance with their bicyclic character and the repulsive forces between the methyl groups. The exocyclic bonds to the methyl C atoms in both molecules are shortened due to the increased s character of the cage C atoms.

Comment

The octamethyl derivative, (III), of *syn*-tricyclo-[$4.2.0.0^{2,5}$]octa-3,7-diene gave octamethylcuneane, (I), and traces of octamethylcubane, (II), among others under irradiation with ultraviolet light (Gleiter & Brand, 1994).

(III)   (I)   (II)
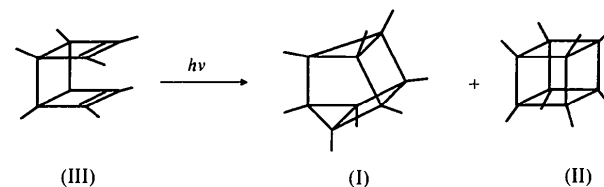
During the course of our studies on strained poly-cyclic compounds (Irngartinger & Strack, 1994), the

extraordinary configurations of three-, four- and five-membered rings based on the cuneane framework seemed worthy of inspection and comparison with their valence isomer octamethylcubane, (II). We therefore investigated the crystal and molecular structure of compounds (I) and (II) from single crystals obtained by slow sublimation.

Compound (I) crystallizes in the centrosymmetric space group $P\bar{1}$ with two molecules in the asymmetric unit, as shown in Fig. 1. The valence isomer, compound (II), crystallizes in the trigonal space group $R\bar{3}m$ and shows a hexagonal close-packing arrangement (Fig. 2). The molecular symmetry of (II) in the crystal is $\bar{3}m$, while the corresponding site symmetry of cubane (Fleischer, 1964) is only $\bar{3}$. Compound (II) has a more spherical shape than cubane.
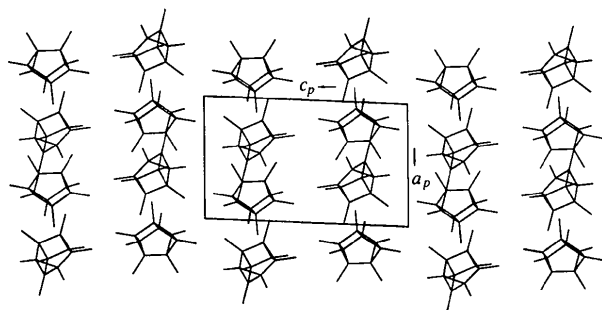

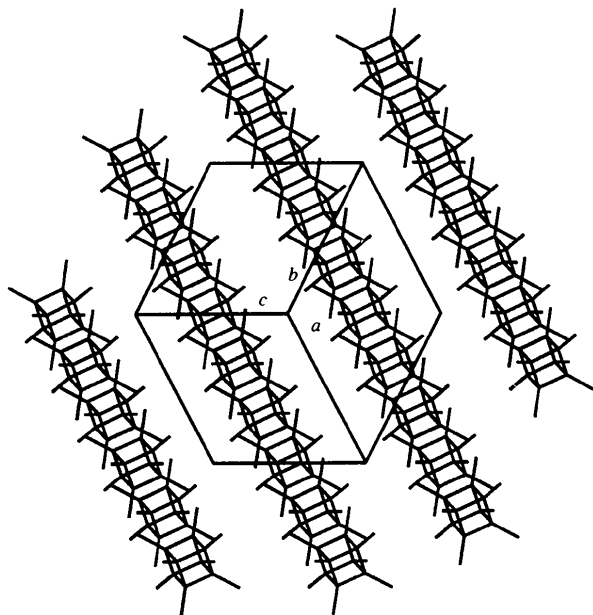Fig. 1. Packing arrangement of octamethylcuneane, (I), as seen along the b axis.

Fig. 2. Packing arrangement of octamethylcubane, (II), as seen along the diagonal [111].

The bond lengths given in Table 2 are the averages of the corresponding chemically equivalent bonds of both independent molecules (Table 1) as illustrated in Fig. 3.

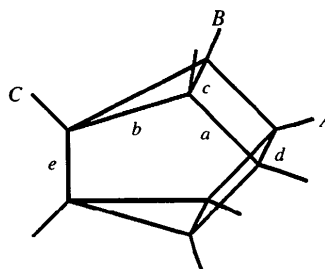The structures of both independent molecules are shown in Fig. 4.

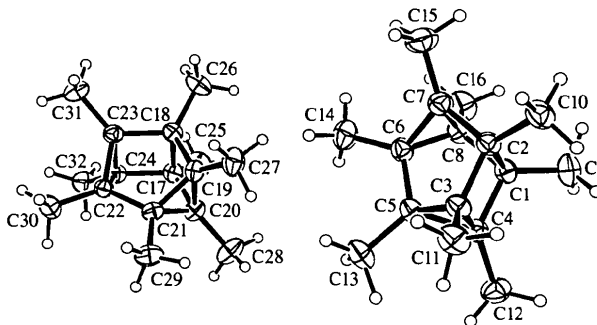Fig. 3. Several types of methyl groups and bonds in (I).

Fig. 4. Structure of octamethylcuneane, (I), with the labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

The methyl groups in position A (Fig. 3) connected with the bond shared by the two four-membered rings are close to an eclipsed orientation [average H₃C—C—C—CH₃ 0.7 (4)°]. Due to the increased s character of the cage C atoms, the exocyclic C—C bonds are shortened to 1.507 (2) Å compared with the average bond lengths of an analogous bond in unstrained hydrocarbons and cyclobutanes (1.530 and 1.529 Å, respectively; Allen et al., 1987). The exocyclic C—CH₃ (B) bonds, with a length of 1.499 (2) Å, are even shorter because three-membered rings in the bicyclo[2.1.0] subunit are involved. The average of the corresponding bond lengths in cyclopropanes is 1.518 Å (Allen et al., 1987). These B-type methyl groups of (I) exhibit an eclipsed orientation with respect to each other [average H₃C—C—C—CH₃ 0.6 (2)°]. The bond shortening of the exocyclic bonds to the methyl groups in position C [1.506 (2) Å] is in the same range as for those in position A. These methyl groups are also nearly eclipsed [average H₃C—C—C—CH₃ 1.1 (5)°]. In cuneane (C₈H₈), the s character for these three types of exocyclic bonds to H atoms at positions A, B and C can be calculated (Muller & Pritchard, 1959) from ¹³C—H coupling constants (Cassar, Eaton & Halpern, 1970) as 30.6, 35.0 and 32.4%, respectively, explaining the relative differences of the shortening effects discussed above.

There are several kinds of bonds (Table 2) in the cuneane cage itself, as illustrated in Fig. 3. The bridging bonds of type a shared by a four- and five-membered

ring with a bond length of 1.551 (3) Å are in the same order of magnitude as the bond lengths in cyclobutanes, 1.554 Å (Allen *et al.*, 1987). The torsion angle between methyl groups of type *A* and *B* is 20.7 (12)°. The bonds *b*, shared by a three- and five-membered ring with a length of 1.520 (2) Å, are shorter than the bond lengths (1.543 Å) of cyclopentane but slightly longer than those (1.510 Å) of cyclopropane (Allen *et al.*, 1987). The bond type *c* shared by a three- and four-membered ring with a length of 1.535 (7) Å is of the same order as that found in housane derivatives (1.532 Å) for an analogous bond (Allen, 1984). Because of the repulsive interactions between the methyl groups in position *A* [average C⋯C 3.126 (4) Å], the bond *d* bearing these groups is lengthened significantly to 1.572 (2) Å compared with the average bond length in cubane (1.551 Å; Fleischer, 1964). The short 1⋯4 distance of 3.062 (5) Å between the methyl groups *C* at bond type *e* gives rise to a lengthening of this bond [1.532 (1) Å] due to the ecliptic position of the methyl groups and the eclipsed conformation of the bicyclopropyl moiety. The repulsive forces are opposed to the effects of higher *s* character at the C atoms of the three-membered ring. The corresponding bond length in unsubstituted bicyclopropyl (Nijveldt & Vos, 1988) is 1.4924 (4) Å. The analogous bond lengths of 1.536 (3) (Quast, Christ, Peters, Peters & von Schnering, 1985) and 1.549 (2) Å (Gleiter, Jähne, Müller, Nixdorf & Irngartinger, 1986) in nortriasterane derivatives are in accordance with our results.

Due to the repulsive interactions between the methyl groups [C1⋯C4 3.310 (4) Å], the average cubane cage bond length of (II) is extended to 1.563 (3) Å (Table 3) compared with 1.551 (3) Å in cubane (Fleischer, 1965). In dimethyl 2,3-dimethylcubane-1,4-dicarboxylate (Cristiano, Gable, Lowe & Tsanaktsidis, 1995), the stretching of the 1,2-disubstituted C—C distance involving the two methyl groups is somewhat longer [1.570 (2) Å] and thus in the range of bond type *d* in the cuneane deriva-

tive, (I). In (II) as in (I), the bond length of the exocyclic C—CH₃ bonds is shortened to 1.507 (5) Å due to the increased *s* character of the cage C atoms in these bonds. The corresponding *s* character in cubane is 30.8% (Della, Hine & Patney, 1977).

Experimental

The synthesis of compounds (I) and (II) is described elsewhere (Gleiter & Brand, 1994). The crystals were grown by slow sublimation.

Compound (I)

Crystal data

$C_{16}H_{24}$	Mo $K\alpha$ radiation
$M_r = 216.37$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 75
$P\bar{1}$	reflections
$a = 8.533$ (1) Å	$\theta = 10.0–24.9°$
$b = 12.044$ (1) Å	$\mu = 0.054$ mm^{-1}
$c = 13.670$ (3) Å	$T = 218$ K
$\alpha = 91.85$ (1)°	Prism
$\beta = 92.11$ (1)°	$0.45 \times 0.40 \times 0.35$ mm
$\gamma = 100.93$ (1)°	Colourless
$V = 1377.4$ (6) Å³	
$Z = 4$	
$D_x = 1.04$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.018$
diffractometer	$\theta_{max} = 27.97°$
$\theta/2\theta$ scans	$h = -11 \rightarrow 11$
Absorption correction: none	$k = -15 \rightarrow 15$
6861 measured reflections	$l = 0 \rightarrow 18$
6587 independent reflections	3 standard reflections
4340 reflections with	frequency: 60 min
$I > 2.5\sigma(I)$	intensity decay: 0.50%

Refinement

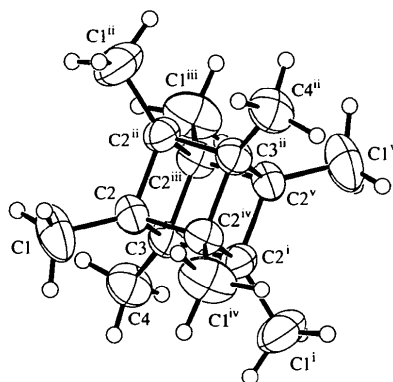|	
Refinement on F^2	$(\Delta/\sigma)_{max} = 0.004$
$R(F) = 0.048$	$\Delta\rho_{max} = 0.2884$ e Å^{-3}
$wR(F^2) = 0.117$	$\Delta\rho_{min} = -0.0764$ e Å^{-3}
$S = 2.446$	Extinction correction: none
4340 reflections	Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
481 parameters	
All H atoms refined	
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0009F_o^4]$	

Fig. 5. Structure of octamethylcubane, (II), with the labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-y$, $x - y$, z; (ii) y, $-x + y$, $-z + 1$; (iii) $-x + y$, $-x$, z; (iv) $x - y$, x, $-z + 1$; (v) $-x$, $-y$, $-z + 1$.]

Table 1. *Selected bond lengths (Å) for (I)*

C1—C2	1.573 (2)	C17—C18	1.570 (2)
C1—C4	1.552 (2)	C17—C20	1.551 (2)
C1—C8	1.553 (2)	C17—C24	1.550 (2)
C2—C3	1.552 (2)	C18—C19	1.548 (2)
C2—C7	1.548 (2)	C18—C23	1.556 (2)
C3—C4	1.535 (2)	C19—C20	1.529 (2)
C3—C5	1.522 (2)	C19—C21	1.519 (2)
C4—C5	1.523 (2)	C20—C21	1.517 (2)
C5—C6	1.532 (2)	C21—C22	1.531 (2)
C6—C7	1.519 (2)	C22—C23	1.521 (2)
C6—C8	1.517 (2)	C22—C24	1.522 (2)
C7—C8	1.531 (2)	C23—C24	1.544 (2)

Table 2. *Bond lengths (Å) of (I) averaged according to the system outlined in Fig. 3*

In brackets, the scatter σ is given by: $\sigma^2 = \Sigma_{i=1}^{n}(x_i - M)^2/(n - 1)$.

Bond type	Length	Bond type	Length
C—C (a)	1.551 (3)	C—CH₃ (A)	1.507 (2)
C—C (b)	1.520 (2)	C—CH₃ (B)	1.499 (2)
C—C (c)	1.535 (7)	C—CH₃ (C)	1.506 (2)
C—C (d)	1.572 (2)		
C—C (e)	1.532 (1)		

Compound (II)

Crystal data

$C_{16}H_{24}$
$M_r = 216.4$
Trigonal
$R\bar{3}m$
$a = 8.562$ (1) Å
$c = 16.833$ (2) Å
$V = 1068.7$ (3) Å³
$Z = 3$
$D_x = 1.01$ Mg m⁻³
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25
reflections
$\theta = 11.7–25.6°$
$\mu = 0.052$ mm⁻¹
$T = 238$ K
Prism
$0.25 \times 0.25 \times 0.15$ mm
Colourless

Data collection

Enraf–Nonius CAD-4
diffractometer
$\theta/2\theta$ scans
Absorption correction: none
978 measured reflections
191 independent reflections
149 reflections with
$I > 2\sigma(I)$

$R_{int} = 0.064$
$\theta_{max} = 24.12°$
$h = -8 \rightarrow 7$
$k = -7 \rightarrow 8$
$l = -4 \rightarrow 19$
3 standard reflections
frequency: 60 min
intensity decay: 1.60%

Refinement

Refinement on F^2
$R(F) = 0.037$
$wR(F^2) = 0.088$
$S = 1.120$
191 reflections
30 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0369P)^2 + 0.2736P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.131$ e Å⁻³
$\Delta\rho_{min} = -0.178$ e Å⁻³
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

C1—C2	1.510 (4)	C2—C3	1.564 (3)
C2—C2ⁱᵛ	1.561 (3)	C3—C4	1.503 (5)
C1—C2—C2ⁱⁱ	125.1 (1)	C2ⁱᵛ—C2—C3	90.3 (1)
C2ⁱᵛ—C2—C2ⁱⁱ	89.9 (2)	C4—C3—C2	125.6 (1)
C1—C2—C3	125.2 (2)	C2—C3—C2ⁱ	89.6 (2)

Symmetry codes: (i) $-y, x - y, z$; (ii) $y, -x+y, -z+1$; (iii) $-x+y, -x, z$; (iv) $x - y, x, -z + 1$; (v) $-x, -y, -z + 1$; as in Fig. 5.

The selection of space groups $P\bar{1}$ and $R\bar{3}m$ for (I) and (II), respectively, was based on statistics of the reflection intensities. H atoms were refined only isotropically. In the crystal of the cuneane derivative, there is a pseudo-twofold screw axis between the two molecules within the asymmetric unit. In the case of some exocyclic methyl groups, this

symmetry relation is subjected to errors up to seven standard deviations. This pseudosymmetry can not be manifested in a crystallographic direction.

For both compounds, data collection: *CAD-4 Manual* (Enraf–Nonius, 1988); cell refinement: *CAD-4 Manual*; data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structures: direct methods (*MULTAN*11/82; Main *et al.*, 1982) for (I); direct methods (*SHELXS*86; Sheldrick, 1985) for (II). Program(s) used to refine structures: *LSFM* in *MolEN* for (I); *SHELXL*93 (Sheldrick, 1993) for (II). For both compounds, molecular graphics: *ORTEP*II (Johnson, 1976) and *SCHAKAL*92 (Keller, 1992); software used to prepare material for publication: *CIF IN* in *MolEN*.

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