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Pentacyclo[9.3.1.1^{2,6}.1^{4,8}.1^{9,13}]octadeca-1(2),8(9)-diene

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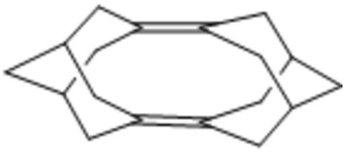
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.043; wR factor = 0.117; data-to-parameter ratio = 10.3.

The title compound, $C_{18}H_{24}$, was the main product of thermolysis of noradamantene dimer (heptacyclo[9.3.1.1^{2,6}.1^{4,8}.1^{9,13}.0^{1,9}.0^{2,8}]octadecane). The crystal structure was determined to prove that the thermolysis product of noradamantene dimer is favored by stretch release due to ring opening of the four-membered ring. The bond length of the quaternary C atoms of the starting material was calculated as 1.6 Å, enlarged in comparison to other single bonds. After the rearrangement, the stretch release of the above carbons leads to an increase of the distance between them (2.824 Å) with respect to the crystallographic data.

Related literature

For reviews on noradamantene and analogous pyramidalized alkenes, see: Borden (1989, 1996); Vázquez & Camps (2005). For the syntheses of noradamantene dimer, see: Renzoni *et al.* (1986) and for related analogs, see: Camps *et al.* (1996*a*,*b*). For the synthesis of the precursor diiodide (3,7-diiodo-tricyclo[3.3.1.0^{3,7}]nonane), an important intermediate in the synthetic route towards the generation of noradamantene, see: Ioannou & Nicolaides (2009). For the synthesis of [2]diadamantane, see: McKervey (1980); Graham *et al.* (1973).



Experimental

Crystal data

$C_{18}H_{24}$
M_r = 240.37
Orthorhombic, *Ccmb*
a = 8.5855 (6) Å
b = 15.6618 (10) Å
c = 9.3156 (6) Å
V = 1252.62 (14) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 100 K
0.15 × 0.07 × 0.04 mm

Data collection

Oxford Diffraction SuperNova Dual (Cu) Atlas diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2008)
T_{min} = 0.530, T_{max} = 1.000
2341 measured reflections
640 independent reflections
514 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.117
S = 1.06
640 reflections
62 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *publCIF* (Westrip (2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZJ2078).

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supplementary materials

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Pentacyclo[9.3.1.1^{2,6}.1^{4,8}.1^{9,13}]octadeca-1(2),8(9)-diene

Savvas Ioannou and Eleni Moushi

Comment

Pyramidalized alkenes is a special category of olefins which have their four substituents of the double bond not lying on the same plane (Borden 1989, 1996, Vázquez & Camps, 2005). This fact makes the higher pyramidalized alkenes (like noradamantene) very reactive and impossible to isolate at ambient conditions. Due to their high reactivity, once they form, they react instantly with any nucleophile. In the absence of any reactive compound during their formation, the most common product is their [2 + 2] dimer. Noradamantene (n=1) is the second member of a homologous series of this category (figure 3) and it can serve as a building block for the formation of larger polycyclic hydrocarbons like the title compound. The most pyramidallized alkene (n=0) of the same homologous series is rearranged spontaneously to the corresponding diene once the dimer is formed (Camps *et al.* 1996a,b) (figure 3). This is attributed to its grater stretch due to the smaller carbon side chain. The title compound is the main product of thermolysis of noradamantene dimer and its formation depends on the reaction conditions. At different reaction conditions (higher temperatures, reaction time) [2]diadamantane (McKervey 1980, Graham *et al.* 1973) and another asymmetric diene were identified among the products.

Experimental

Synthesis of pentacyclo [9.3.1.1^{2,6}.1^{4,8}.1^{9,13}] octadeca-di-1(2),8(9)-ene. Heptacyclo [9.3.1.1^{2,6}.1^{4,8}.1^{9,13}.0^{1,9}.0^{2,8}] octadecane-(10 mg,0.042 mmol) was placed in a cylindrical glass container with small diameter (~5 mm suitable for glass workshops) sealed at the bottom edge, while the other edge was connected at the vacuum line. The glass cylinder was washed three times with argon and placed under vacuum for 5 minutes after which the opened edge was sealed as well with the use of a flamethrower, encapsulating the reactant under vacuum. The capsule was placed in a controlled temperature oven at 350 ^{o}C for 5 minutes. Crystals of the product and the reactant were formed when the capsule cooled down to room temperature. The starting material was removed by breaking carefully the glass of the one edge and washing the solid with hexane 3x1 ml. The residue was mostly product which was recrystallized by sealing the capsule again under vacuum and reheating it at 350°C for another 5 minutes. Colorless crystals of pure product were formed when the capsule cooled down to room temperature.

Refinement

The H atoms are positioned with idealized geometry and refined using a riding model with $U_{\rm iso}$(H) = 1.2 of $U_{\rm eq}$ (C).

Computing details

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis CCD* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED* (Oxford Diffraction, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1999) and Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *publCIF* (Westrip (2010).

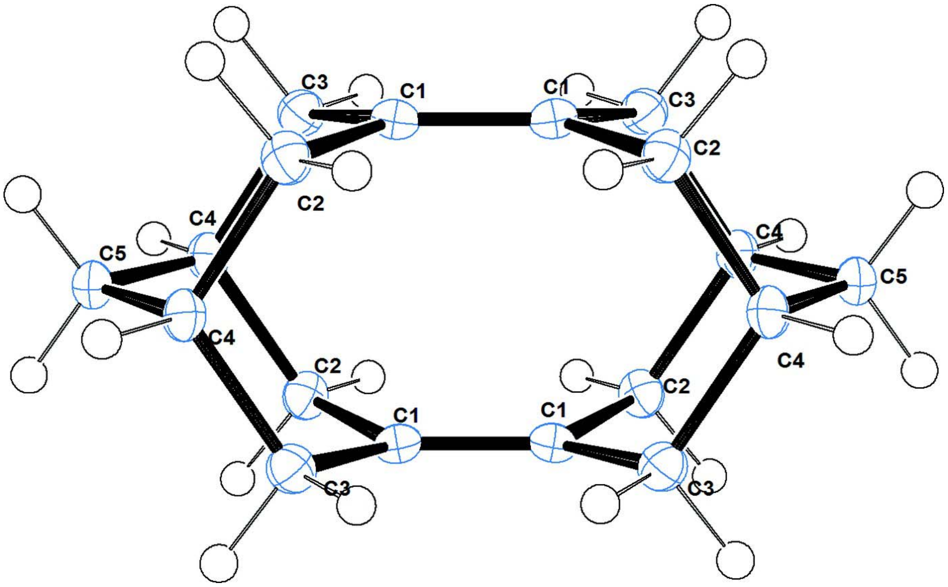

Figure 1

Structure of the title compound pentacyclo [9.3.1.1^{2,6}.1^{4,8}.1^{9,13}] octadeca-di-1(2),8(9)-ene with the atom-labelling. Displacement elipsoids are drawn at the 50% probability level.

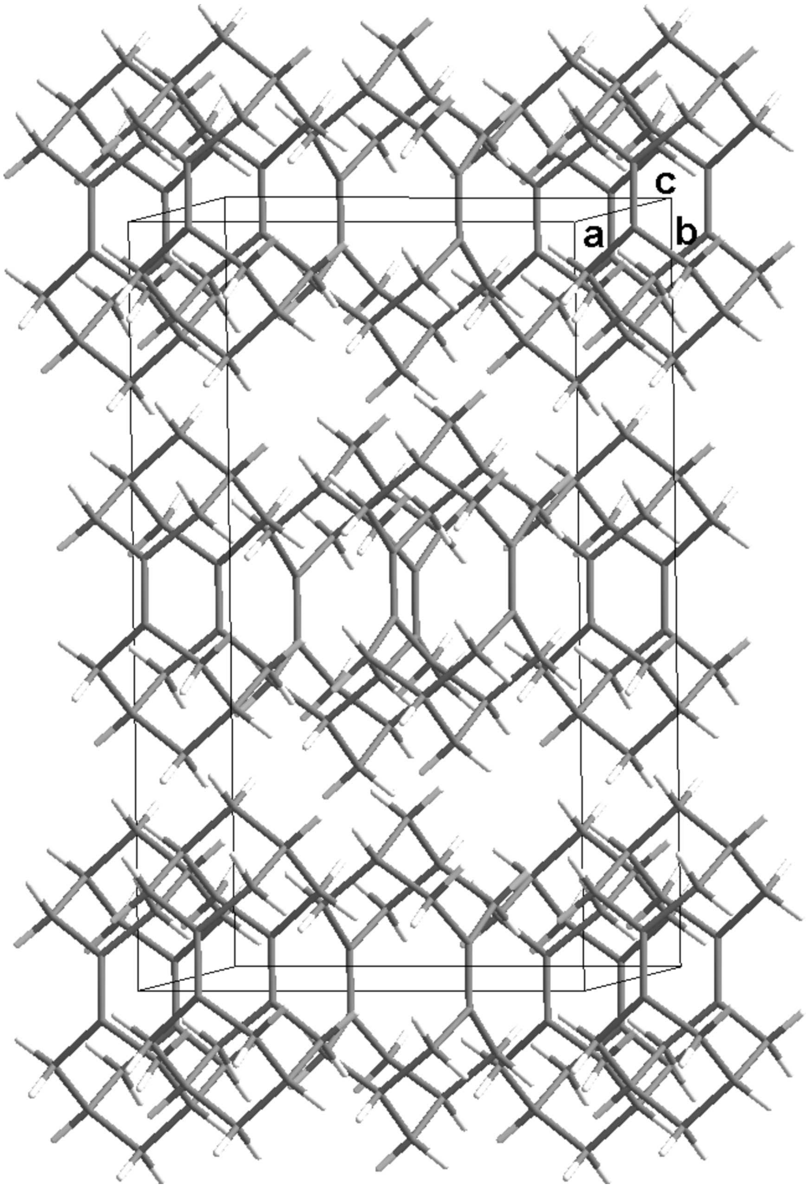

Figure 2

Molecular packing of the title compound, viewed along [1 0 0].

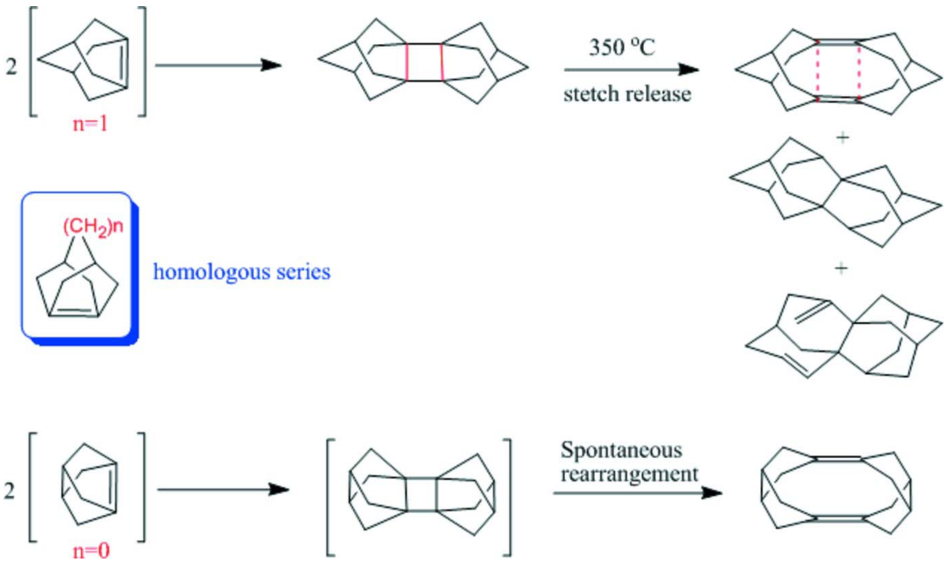

Figure 3

Dimer rearrangement of the two first members of a homologous series of pyramidalized alkenes.

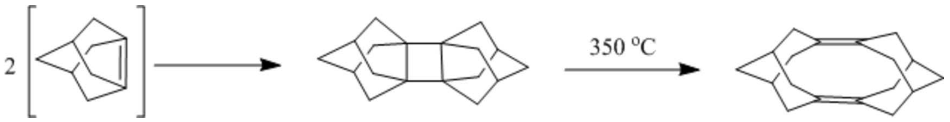

Figure 4

The formation of the title compound.

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Crystal data

$C_{18}H_{24}$
M_r = 240.37
Orthorhombic, *Ccmb*
Hall symbol: -C 2bc 2bc
a = 8.5855 (6) Å
b = 15.6618 (10) Å
c = 9.3156 (6) Å
V = 1252.62 (14) Å^3
Z = 4

F(000) = 528
D_x = 1.275 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 1022 reflections
θ = 3.4–28.9°
μ = 0.07 mm^{-1}
T = 100 K
Polyhedral, colorless
0.15 × 0.07 × 0.04 mm

Data collection

Oxford Diffraction SuperNova Dual (Cu) Atlas diffractometer
Radiation source: SuperNova (Mo) X-ray Source
Mirror monochromator
Detector resolution: 10.4223 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2008)

T_{min} = 0.530, T_{max} = 1.000
2341 measured reflections
640 independent reflections
514 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 26.0°, θ_{min} = 3.5°
$h = -10 \rightarrow 9$
$k = -19 \rightarrow 18$
$l = -11 \rightarrow 8$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.117$
$S = 1.06$
640 reflections
62 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2 + 0.8624P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.44$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.11524 (14)	0.04287 (9)	0.10813 (13)	0.0158 (4)	
C2	0.00121 (16)	0.09715 (9)	0.19231 (15)	0.0180 (4)	
C3	0.20910 (17)	0.09726 (9)	0.00491 (15)	0.0178 (4)	
C4	−0.10310 (16)	0.15159 (9)	0.09316 (15)	0.0177 (4)	
C5	0.0000	0.20830 (13)	0.0000	0.0190 (5)	
H5A	0.0641	0.2446	0.0603	0.023*	0.50
H5B	−0.0641	0.2446	−0.0603	0.023*	0.50
H2A	−0.0646 (17)	0.0622 (11)	0.2559 (18)	0.024 (4)*	
H2B	0.0618 (18)	0.1376 (11)	0.256 (2)	0.032 (4)*	
H3A	0.2779 (19)	0.1360 (11)	0.0608 (17)	0.028 (4)*	
H3B	0.2842 (18)	0.0618 (11)	−0.0514 (15)	0.023 (4)*	
H4	−0.1732 (16)	0.1880 (9)	0.1554 (15)	0.012 (3)*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0144 (7)	0.0184 (7)	0.0147 (7)	0.0009 (5)	−0.0028 (5)	0.0008 (6)
C2	0.0205 (8)	0.0174 (8)	0.0161 (7)	0.0012 (6)	0.0007 (6)	−0.0008 (6)
C3	0.0162 (7)	0.0180 (8)	0.0192 (8)	−0.0013 (6)	0.0001 (6)	0.0012 (6)
C4	0.0192 (7)	0.0140 (7)	0.0201 (7)	0.0025 (5)	−0.0002 (6)	−0.0043 (6)
C5	0.0223 (10)	0.0120 (10)	0.0228 (10)	0.000	−0.0051 (8)	0.000

Geometric parameters (Å, º)

C1—C1^{i}	1.343 (3)	C3—H3B	1.000 (16)
C1—C2	1.5153 (18)	C4—C5	1.5250 (17)
C1—C3	1.5164 (18)	C4—C3^{ii}	1.5450 (19)
C2—C4	1.5434 (18)	C4—H4	1.012 (14)
C2—H2A	0.984 (17)	C5—C4^{ii}	1.5250 (17)
C2—H2B	1.009 (18)	C5—H5A	0.9700
C3—C4^{ii}	1.5450 (19)	C5—H5B	0.9700
C3—H3A	0.994 (17)		
C1^{i}—C1—C2	124.13 (7)	H3A—C3—H3B	103.3 (13)
C1^{i}—C1—C3	124.17 (7)	C5—C4—C2	109.00 (11)
C2—C1—C3	110.88 (11)	C5—C4—C3^{ii}	109.04 (11)
C1—C2—C4	112.03 (11)	C2—C4—C3^{ii}	113.04 (11)
C1—C2—H2A	111.7 (10)	C5—C4—H4	110.1 (8)
C4—C2—H2A	109.5 (9)	C2—C4—H4	108.3 (8)
C1—C2—H2B	108.7 (9)	C3^{ii}—C4—H4	107.4 (8)
C4—C2—H2B	107.6 (10)	C4—C5—C4^{ii}	108.75 (15)
H2A—C2—H2B	107.0 (15)	C4—C5—H5A	109.9
C1—C3—C4^{ii}	111.80 (11)	C4^{ii}—C5—H5A	109.9
C1—C3—H3A	109.1 (9)	C4—C5—H5B	109.9
C4^{ii}—C3—H3A	108.9 (9)	C4^{ii}—C5—H5B	109.9
C1—C3—H3B	111.3 (9)	H5A—C5—H5B	108.3
C4^{ii}—C3—H3B	112.1 (9)		

Symmetry codes: (i) $x, -y, z$; (ii) $-x, y, -z$.