

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

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

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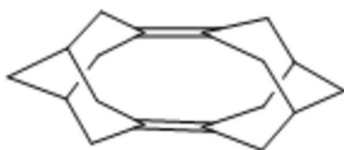
Received 9 May 2012; accepted 13 June 2012

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å;
R factor = 0.043; wR factor = 0.117; data-to-parameter ratio = 10.3.

The title compound, $\text{C}_{18}\text{H}_{24}$, 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: McKervery (1980); Graham *et al.* (1973).



Experimental

Crystal data

$\text{C}_{18}\text{H}_{24}$	$V = 1252.62$ (14) Å ³
$M_r = 240.37$	$Z = 4$
Orthorhombic, <i>Cc</i>	Mo $K\alpha$ radiation
$a = 8.5855$ (6) Å	$\mu = 0.07$ mm ⁻¹
$b = 15.6618$ (10) Å	$T = 100$ K
$c = 9.3156$ (6) Å	$0.15 \times 0.07 \times 0.04$ mm

Data collection

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

Refinement

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

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)).

We are grateful to the Research Promotion Foundation (ΙΠΕ) of Cyprus and the European Structural Funds for grant ANABAΘ/ΠΑΓΙΟ/0308/12 which allowed the purchase of the XRD instrument, NEKYΠ/0308/02 enabling the purchase of a 500 MHz NMR spectrometer, of the RSC journal archive and for access to Reaxys and financial support to SI (ΠΕΝΕΚ/ΕΝΙΣΧ/0308/01). Partial financial support (SI) was also provided by the SRP "Interesting Divalent Carbon Compounds" granted by UCY. The A. G. Leventis Foundation is gratefully acknowledged for a generous donation to the University of Cyprus enabling the purchase of the 300 MHz NMR spectrometer. Dr Athanassios Nicolaides and Dr Anastasios Tasiopoulos are thanked for their illuminating comments.

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

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supporting information

Acta Cryst. (2012). E68, o2150 [https://doi.org/10.1107/S1600536812026785]

Pentacyclo[9.3.1.1^{2,6}.1^{4,8}.1^{9,13}]octadeca-1(2),8(9)-diene**Savvas Ioannou and Eleni Moushi****S1. 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 pyramidalized 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 greater 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.

S2. 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 °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.

S3. Refinement

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

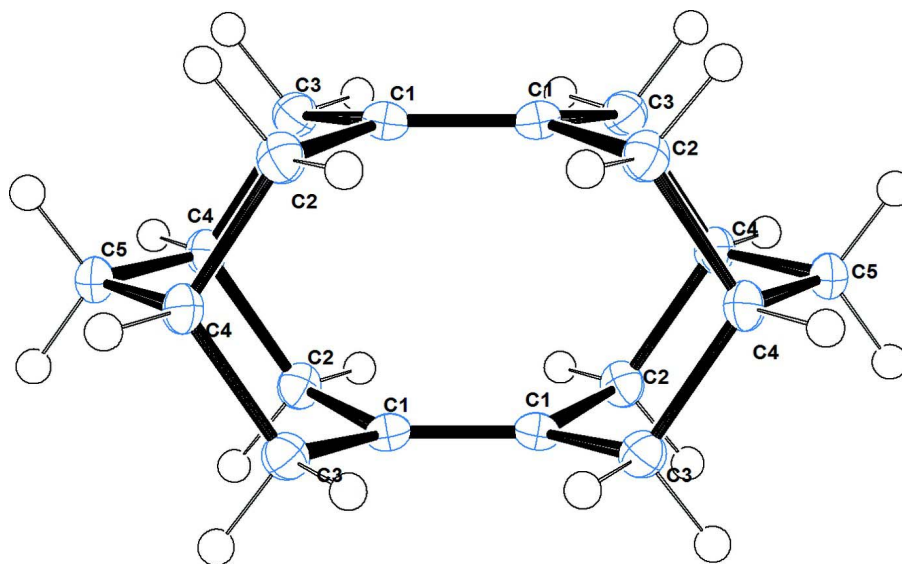


Figure 1

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 ellipsoids are drawn at the 50% probability level.

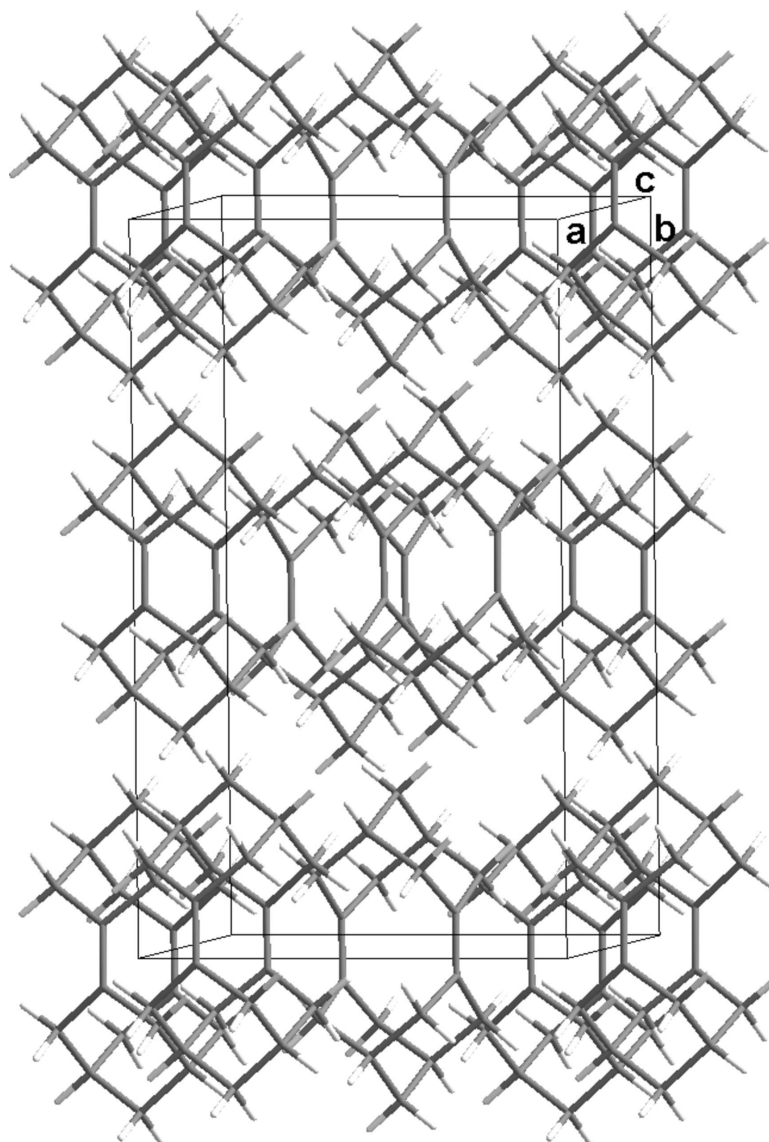
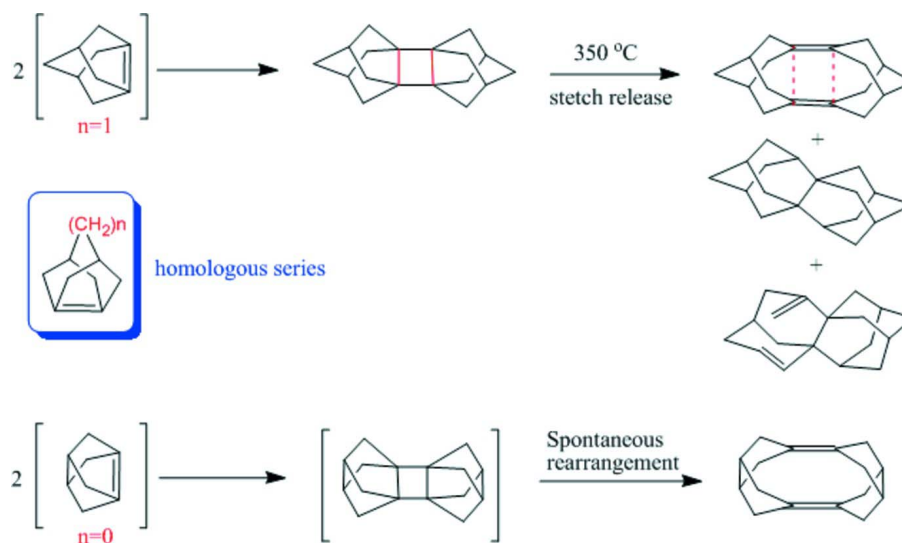
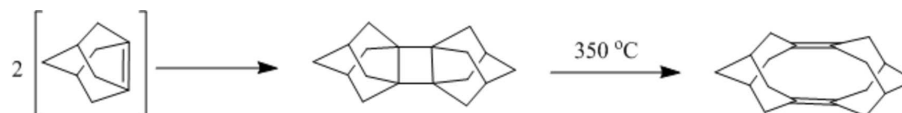


Figure 2

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.

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

Crystal data

$C_{18}H_{24}$

$M_r = 240.37$

Orthorhombic, *Cc*

Hall symbol: -C 2bc 2bc

$a = 8.5855$ (6) Å

$b = 15.6618$ (10) Å

$c = 9.3156$ (6) Å

$V = 1252.62$ (14) Å³

$Z = 4$

$F(000) = 528$

$D_x = 1.275$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1022 reflections

$\theta = 3.4$ – 28.9°

$\mu = 0.07$ mm⁻¹

$T = 100$ K

Polyhedral, colorless

$0.15 \times 0.07 \times 0.04$ 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 $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 3.5^\circ$

$h = -10 \rightarrow 9$

$k = -19 \rightarrow 18$

$l = -11 \rightarrow 8$

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 $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.44 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.16 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	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 (\AA^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 (\AA , $^\circ$)

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) $-x, y, -z$.