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All-*E*-7,8,9,10,11,12-hexaethyl[6]radialene†

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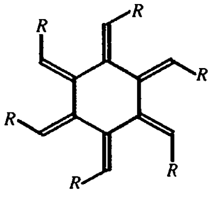
Abstract

The title compound, $C_{24}H_{36}$, displays crystallographic inversion symmetry, but the actual symmetry is close to $\bar{3}$. The structure is closely similar to, but not isostructural with, the analogous hexamethyl derivative [Marsh & Dunitz (1975). *Helv. Chim. Acta*, **58**, 707–712]. The ring adopts a chair conformation with absolute torsion angles in the range 45.4 (4)–45.8 (4)°. Ring bond lengths are 1.480 (4)–1.500 (4) Å and ring bond angles are 113.9 (3)–114.8 (3)°.

Comment

As part of our current investigations on cross-conjugated π-systems, we were interested in the structure of all-*E*-7,8,9,10,11,12-hexaethyl[6]radialene, (2) (for a review of radialenes see Hopf & Maas, 1992). X-ray structural investigations of the conformation of the cyclohexane ring in [6]radialenes have revealed both planar and non-planar geometries; annelated systems are generally planar, whereas unbridged systems are generally planar when the substituents are solely diazo and keto, and otherwise non-planar (Jones, Ahrens, Höpfner & Hopf, 1997, and references therein). The X-ray structure of the hexamethyl derivative, (1), was determined by Marsh & Dunitz (1975), revealing a molecule with crystallographic inversion symmetry (effective symmetry $\bar{3}$) and a chair conformation (torsion angles alternating ±46.2°). A recent gas-phase electron-diffraction study (Benet-Buchholz, Boese, Hauman & Traetteberg, 1997) found the bond lengths and angles to be in good agreement with those of Marsh & Dunitz (1975); however, the torsion angles in the gas phase were appreciably greater at 53.0°. To obtain further information about such systems, we have now investigated the solid-state structure of (2), the next higher homologue of (1).



(1) R = Me
(2) R = Et

Despite the lower measurement temperature the structure of (2) is slightly less precise than that of (1); this can be attributed to the greater displace-

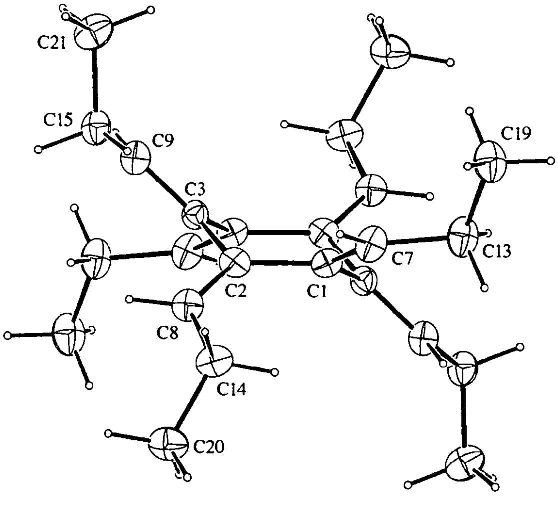


Fig. 1. The molecule of the title compound in the crystal. Ellipsoids represent 30% probability levels. Only the asymmetric unit is numbered. H-atom radii are arbitrary.

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† Alternative name: (1*E*,2*E*,3*E*,4*E*,5*E*,6*E*)-1,2,3,4,5,6-hexakis(propylidene)cyclohexane.

ment parameters of the terminal atoms and consequent weaker diffraction. However, the main features of (1) and (2) are essentially identical. The crystallographic symmetry of (2) is $\bar{1}$, but the actual symmetry is close to $\bar{3}$. Bond lengths in the ring are 1.480 (4)–1.500 (4) Å [values for (1) in square brackets: 1.493 (3)–1.495 (2) Å]; ring bond angles 113.9 (3)–114.8 (3)° [114.1 (1)–114.2 (2)°]; absolute ring torsion angles 45.4 (4)–45.8 (4)° [all 46.2°]; C═C 1.336 (5)–1.347 (4)° [1.332 (2)–1.337 (3)°]. The exocyclic C_{sp^2}—C_{sp^3} bonds, 1.480 (5)–1.494 (4) Å [1.497 (3)–1.499 (4) Å], are not significantly different in length from their endocyclic counterparts. The outermost C—C single bonds, 1.510 (5)–1.516 (5) Å, are necessarily longer, although their true lengths may be masked by libration effects. Unsurprisingly, rigid-body libration corrections proved ineffective.

Experimental

The title compound was obtained by a known procedure (Hopff & Gati, 1965). Spectroscopic data: ^{1}H NMR ($CDCl_3$, Bruker AM 400): $\delta = 5.20$ (*t*, $^3J = 7.3$ Hz, 6H, =$CHCH_2$), 2.22 (quint, $^3J = 7.4$ Hz, 12H, CH_2), 1.02 (*t*, $^3J = 7.5$ Hz, 18H, CH_3); ^{13}C NMR ($CDCl_3$, Bruker AM 400): $\delta = 138.77$ (*s*, ring-C), 127.69 (*d*, =CH), 22.08 (*t*, CH_2), 15.08 (*q*, CH_3); IR (KBr, Nicolet FT-IR 320): $\nu = 3018$ (*m*), 3001 (*m*), 2963 (*s*), 2931 (*s*), 2908 (*m*), 2871 (*s*), 2841 (*m*), 1736 (*w*), 1719 (*w*), 1708 (*w*), 1702 (*w*), 1654 (*w*), 1648 (*w*), 1638 (*w*), 1620 (*w*), 1459 (*m*), 1440 (*w*), 1431 (*w*), 1376 (*m*), 1351 (*w*), 1303 (*w*), 1152 (*w*), 1068 (*m*), 1041 (*w*), 1031 (*w*), 915 (*m*), 878 (*m*), 850 (*m*), 765 (*m*), 713 (*w*), 644 (*w*); UV/visible (hexane, HP 8452 A Diode Array Spectrophotometer): λ_{max} (log ε) = 208 nm (4.543). Crystallization from acetone yielded single crystals suitable for X-ray diffraction.

Crystal data

$C_{24}H_{36}$
$M_r = 324.53$
Monoclinic
$C2/c$
$a = 19.578$ (5) Å
$b = 14.508$ (3) Å
$c = 7.979$ (2) Å
$\beta = 106.21$ (2)°
$V = 2176.2$ (9) Å^3
$Z = 4$
$D_x = 0.991$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 47 reflections
$\theta = 10.0$–11.5°
$\mu = 0.055$ mm^{-1}
$T = 178$ (2) K
Prism
0.50 × 0.30 × 0.20 mm
Colourless

Data collection

Nicolet *R*3 diffractometer
ω scans
Absorption correction: none
3602 measured reflections
1930 independent reflections
1048 reflections with $I > 2\sigma(I)$
$R_{int} = 0.072$

$\theta_{max} = 25.06°$
$h = -23 \rightarrow 0$
$k = -17 \rightarrow 12$
$l = -9 \rightarrow 9$
3 standard reflections every 147 reflections intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.221$
$S = 1.008$
1930 reflections
112 parameters
H atoms: rigid methyls, others riding

$w = 1/[\sigma^2(F_o^2) + (0.0893P)^2 + 3.6393P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.352$ e Å^{-3}
$\Delta\rho_{min} = -0.220$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C1—C7	1.344 (5)	C7—C13	1.482 (5)
C1—C2	1.480 (4)	C8—C14	1.480 (5)
C1—C3^i	1.500 (4)	C9—C15	1.494 (4)
C2—C8	1.347 (4)	C13—C19	1.510 (5)
C2—C3	1.486 (5)	C14—C20	1.515 (5)
C3—C9	1.336 (5)	C15—C21	1.516 (5)
C7—C1—C2—C8	−54.2 (5)	C2—C3—C9—C15	0.7 (6)
C3^i—C1—C2—C3	−45.8 (4)	C1—C7—C13—C19	136.3 (4)
C8—C2—C3—C9	53.8 (5)	C2—C8—C14—C20	−132.2 (4)
C1—C2—C3—C1^i	45.6 (4)	C3—C9—C15—C21	130.2 (4)
C3^i—C1—C7—C13	−0.3 (6)	C2—C1—C3^i—C2^i	45.4 (4)
C1—C2—C8—C14	0.0 (5)		

Symmetry code: (i) $\frac{1}{2} - x, \frac{3}{2} - y, -z$.

Data collection: *P*3 (Nicolet XRD Corporation, 1987). Cell refinement: *P*3. Data reduction: *XDISK* in *P*3. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1289). Services for accessing these data are described at the back of the journal.

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