

(1*E*,5*E*)-2,5-Dibromocyclododeca-1,5-dien-9-yne

Heiner Detert* and Dieter Schollmeyer

University of Mainz, Institut of Organic Chemistry, Duesbergweg 10-14, 55099 Mainz, Germany. *Correspondence e-mail: detert@uni-mainz.de

Received 11 September 2017

Accepted 24 October 2017

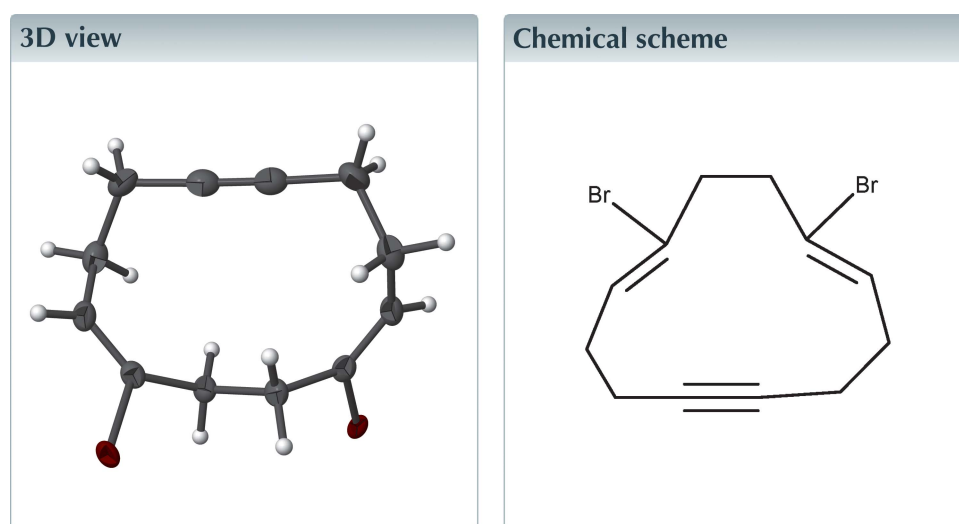
Edited by W. T. A. Harrison, University of Aberdeen, Scotland

Keywords: crystal structure; organobromine compound; cycloalkyne.

CCDC reference: 1581763

Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{12}H_{14}Br_2$, was prepared by bromination/dehydrobromination of *E,E,Z*-cyclododecatriene. The crystal is composed of C_2 -symmetrical molecules with an *E* conformation of the bromoalkene fragments and nearly linear alkyne units. The torsion angles in the ring suggest significant ring strain.



Structure description

Dibromocyclododecatriene has been prepared as intermediate for the selective synthesis of (*Z,Z,Z*)-cyclododecatriene (Trauer & Haufe, 1988) and cyclotridecatrienes (Trauer & Haufe, 1990). The former is a valuable intermediate for the preparation of cyclododecatriyne (Barkovich & Vollhardt, 1976) and hexaradialene (Barkovich *et al.* 1980). Currently, strained alkynes are central coupling partners in click chemistry. Even medium-sized cycloalkynes can be highly strained (Meier *et al.* 1982; Bissinger *et al.* 1988).

The orthorhombic unit cell of the title compound (Fig. 1) is filled with four identical molecules of C_2 symmetry: the X-ray analysis gives proof for the *E*-conformation of the bromovinylene units. The C_2 -symmetrical molecule shows a nearly perfect linearity of the alkyne unit with bond angles at the sp carbon atoms of $178.4(4)^\circ$. Whereas the ethylene unit $C1-C1^i$ [symmetry code: (i) $-x, y, -z + \frac{1}{2}$] possesses quasi ideal bond and torsion angles, the bond angles at $C4$ [$C3-C4-C5 = 112.0(6)^\circ$] and $C5$ [$C4-C5-C6 = 113.9(6)^\circ$] are slightly opened. The same holds for the sp^2 carbon atoms [$C3-C2-C1 = 128.0(6)^\circ$]. These deformations and the torsion angles $C2-C3-C4-C5 = -102.7(8)$ and $C3-C4-C5-C6 = 73.4(8)^\circ$ indicate geometrical ring strain even in a macrocyclic alkyne. In the crystal (Fig. 2), no directional interactions beyond normal van der Waals contacts could be identified.

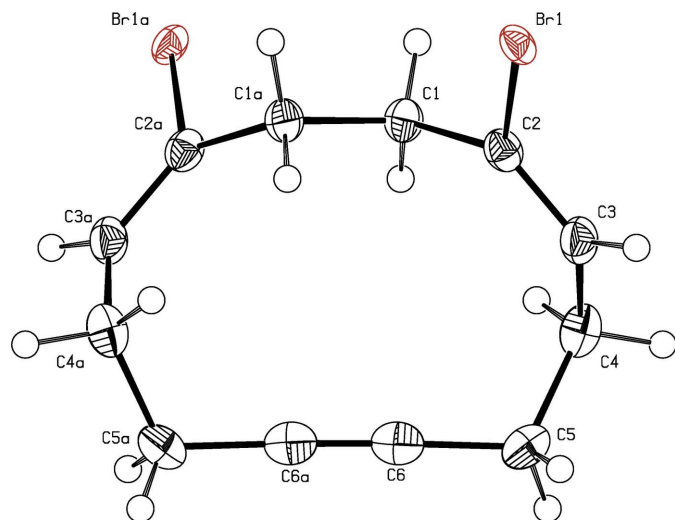


Figure 1
View of the title compound. Displacement ellipsoids are drawn at the 50% probability level. Atoms with the suffix a are generated by the symmetry operation $-x, y, -z + \frac{1}{2}$.

Synthesis and crystallization

The title compound was prepared in a two-step procedure. First, 40.5 g (0.25 mol) of *E,E,Z*-1,5,9-cyclododecatriene in a Morton flask (2 l) containing 1 l anhydrous ether was cooled in an ice bath (CaCl₂ tube). A solution of 120.0 g, of bromine (0.75 mol) in dichloromethane in a constant addition funnel with Mariott tube (NORMAG) was added dropwise to the heavily stirred solution. When the colour vanished, 100 ml of petroleum ether was added slowly and the precipitate was collected on a Büchner funnel, yield: 132.8 g (83%) of a white powder with m.p. 471 K. Dehydrobromination of 6.4 g of the

Table 1
Experimental details.

Crystal data	
Chemical formula	C ₁₂ H ₁₄ Br ₂
<i>M_r</i>	318.05
Crystal system, space group	Orthorhombic, <i>Pbcn</i>
Temperature (K)	120
<i>a</i> , <i>b</i> , <i>c</i> (Å)	16.8714 (12), 7.7191 (4), 9.1556 (5)
<i>V</i> (Å ³)	1192.35 (12)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	6.76
Crystal size (mm)	0.27 × 0.23 × 0.22
Data collection	
Diffractometer	Stoe IPDS 2T
Absorption correction	Integration (<i>X-RED32</i> ; Stoe & Cie, 2006b)
<i>T_{min}</i> , <i>T_{max}</i>	0.190, 0.356
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	7295, 1465, 1204
<i>R_{int}</i>	0.031
(sin θ/λ) _{max} (Å ⁻¹)	0.665
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.061, 0.193, 1.20
No. of reflections	1465
No. of parameters	64
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.54, -0.69

Computer programs: *X-AREA* and *X-RED32* (Stoe & Cie, 2006), *SHELXT2014* (Sheldrick, 2015a) and *SHELXL2017* (Sheldrick, 2015b).

hexabromocyclododecane with sodium ethanolate in ethanol was performed according to Trauer & Haufe (1988) and yielded 2.13 g (65%) of an off-white powder with m.p. 431 K. Colourless blocks were grown *via* slow evaporation of a solution in chloroform and 2-propanol (1:1).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

References

- Barkovich, A. J., Strauss, E. S. & Vollhardt, K. P. C. (1980). *Isr. J. Chem.* **20**, 225–232.
- Barkovich, A. J. & Vollhardt, K. P. C. (1976). *J. Am. Chem. Soc.* **98**, 2667–2668.
- Bissinger, H. J., Detert, H. & Meier, H. (1988). *Liebigs Ann. Chem.* pp. 221–224.
- Meier, H., Molz, T., Merkle, U., Echter, T. & Lorch, M. (1982). *Liebigs Ann. Chem.* pp. 914–923.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Stoe & Cie (2006). *X-AREA* and *X-RED32*. Stoe & Cie, Darmstadt, Germany.
- Trauer, H. & Haufe, G. (1988). *Z. Chem.* **28**, 290–291.
- Trauer, H. & Haufe, G. (1990). *J. Chem. Res. (S)*, **7**, 210–211.

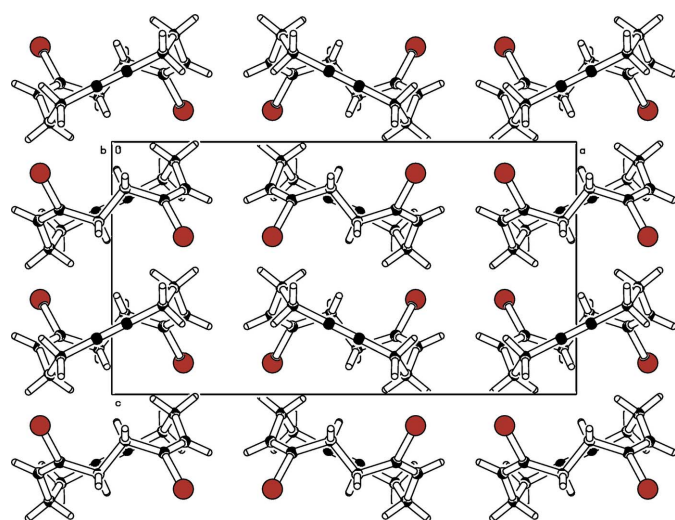


Figure 2
Part of the packing diagram. View along *b*-axis direction.

full crystallographic data

IUCrData (2017). 2, x171550 [https://doi.org/10.1107/S2414314617015504]

(1*E*,5*E*)-2,5-Dibromocyclododeca-1,5-dien-9-yne

Heiner Detert and Dieter Schollmeyer

(1*E*,5*E*)-2,5-Dibromocyclododeca-1,5-dien-9-yne*Crystal data*

$C_{12}H_{14}Br_2$

$M_r = 318.05$

Orthorhombic, *Pbcn*

$a = 16.8714$ (12) Å

$b = 7.7191$ (4) Å

$c = 9.1556$ (5) Å

$V = 1192.35$ (12) Å³

$Z = 4$

$F(000) = 624$

$D_x = 1.772$ Mg m⁻³

Melting point: 431 K

Mo *K*α radiation, $\lambda = 0.71073$ Å

Cell parameters from 9463 reflections

$\theta = 2.4$ – 28.4°

$\mu = 6.76$ mm⁻¹

$T = 120$ K

Block, colourless

$0.27 \times 0.23 \times 0.22$ mm

Data collection

Stoe IPDS 2T
diffractometer

Radiation source: sealed X-ray tube, 12 x 0.4
mm long-fine focus

Plane graphite monochromator

Detector resolution: 6.67 pixels mm⁻¹

rotation method scans

Absorption correction: integration
(X-RED32; Stoe & Cie, 2006b)

$T_{\min} = 0.190$, $T_{\max} = 0.356$

7295 measured reflections

1465 independent reflections

1204 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\max} = 28.2^\circ$, $\theta_{\min} = 2.4^\circ$

$h = -22 \rightarrow 22$

$k = -10 \rightarrow 10$

$l = -11 \rightarrow 12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.061$

$wR(F^2) = 0.193$

$S = 1.20$

1465 reflections

64 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0757P)^2 + 11.4374P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.54$ e Å⁻³

$\Delta\rho_{\min} = -0.69$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Hydrogen atoms attached to carbons were placed at calculated positions with C—H = 0.95 Å (sp^2) or 0.99 Å (sp^3 C-atom). All H atoms were refined in the riding-model approximation with isotropic displacement parameters (set at 1.2–1.5 times of the U_{eq} of the parent atom).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
Br1	0.15412 (3)	0.49337 (7)	0.37567 (6)	0.0204 (3)
C1	0.0288 (3)	0.3816 (8)	0.1832 (7)	0.0243 (12)
H1A	0.010594	0.295662	0.110314	0.029*
H1B	0.028447	0.497259	0.136454	0.029*
C2	0.1119 (3)	0.3376 (8)	0.2315 (7)	0.0223 (12)
C3	0.1575 (3)	0.2044 (9)	0.1877 (8)	0.0265 (13)
H3	0.208538	0.193789	0.230594	0.032*
C4	0.1342 (4)	0.0716 (9)	0.0768 (8)	0.0300 (14)
H4A	0.179279	0.051056	0.009796	0.036*
H4B	0.089357	0.116479	0.018263	0.036*
C5	0.1100 (5)	−0.1000 (9)	0.1478 (8)	0.0339 (16)
H5A	0.109077	−0.191212	0.071789	0.041*
H5B	0.150743	−0.132693	0.220615	0.041*
C6	0.0324 (4)	−0.0948 (8)	0.2201 (8)	0.0305 (14)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0147 (4)	0.0213 (4)	0.0251 (4)	−0.00532 (19)	−0.0026 (2)	0.00172 (19)
C1	0.017 (2)	0.026 (3)	0.031 (3)	0.001 (2)	−0.002 (3)	0.001 (3)
C2	0.020 (3)	0.025 (3)	0.022 (3)	−0.002 (2)	−0.001 (2)	0.005 (2)
C3	0.018 (3)	0.031 (3)	0.031 (3)	0.002 (2)	0.001 (2)	0.005 (3)
C4	0.025 (3)	0.039 (4)	0.025 (3)	0.005 (3)	0.002 (3)	−0.001 (3)
C5	0.033 (4)	0.027 (3)	0.042 (4)	0.009 (3)	0.004 (3)	−0.001 (3)
C6	0.038 (3)	0.025 (3)	0.029 (3)	−0.001 (3)	−0.002 (3)	0.000 (3)

Geometric parameters (Å, °)

Br1—C2	1.922 (6)	C4—C5	1.531 (11)
C1—C2	1.509 (8)	C4—H4A	0.9900
C1—C1 ⁱ	1.562 (12)	C4—H4B	0.9900
C1—H1A	0.9900	C5—C6	1.469 (10)
C1—H1B	0.9900	C5—H5A	0.9900
C2—C3	1.346 (9)	C5—H5B	0.9900
C3—C4	1.495 (10)	C6—C6 ⁱ	1.222 (14)
C3—H3	0.9500		
C2—C1—C1 ⁱ	110.4 (6)	C3—C4—H4A	109.2
C2—C1—H1A	109.6	C5—C4—H4A	109.2
C1 ⁱ —C1—H1A	109.6	C3—C4—H4B	109.2
C2—C1—H1B	109.6	C5—C4—H4B	109.2

C1 ⁱ —C1—H1B	109.6	H4A—C4—H4B	107.9
H1A—C1—H1B	108.1	C6—C5—C4	113.9 (6)
C3—C2—C1	128.0 (6)	C6—C5—H5A	108.8
C3—C2—Br1	118.1 (5)	C4—C5—H5A	108.8
C1—C2—Br1	113.9 (4)	C6—C5—H5B	108.8
C2—C3—C4	125.2 (6)	C4—C5—H5B	108.8
C2—C3—H3	117.4	H5A—C5—H5B	107.7
C4—C3—H3	117.4	C6 ⁱ —C6—C5	178.4 (4)
C3—C4—C5	112.0 (6)		
C1 ⁱ —C1—C2—C3	120.5 (6)	Br1—C2—C3—C4	-179.9 (5)
C1 ⁱ —C1—C2—Br1	-58.5 (4)	C2—C3—C4—C5	-102.7 (8)
C1—C2—C3—C4	1.2 (11)	C3—C4—C5—C6	73.4 (8)

Symmetry code: (i) $-x, y, -z+1/2$.