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4,12-Bis(2,2-dibromovinyl)[2.2]-paracyclophane

Sébastien Clément,^a Laurent Guyard,^a Michael Knorr,^a Christian Däschlein^b and Carsten Strohmann^{b*}

^aInstitut UTINAM UMR CNRS 6213, Université de Franche-Comté, 16 Route de Gray, La Bouloie, 25030 Besançon, France, and ^bTechnische Universität Dortmund, Anorganische Chemie Otto-Hahn-Strasse 6, D-44227 Dortmund, Germany
Correspondence e-mail: carsten.strohmamm@tu-dortmund.de

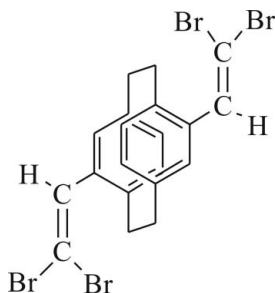
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Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.032; wR factor = 0.073; data-to-parameter ratio = 18.7.

In the title compound, $\text{C}_{20}\text{H}_{16}\text{Br}_4$, both vinylic substituents were introduced by a Corey–Fuchs reaction using 4,12-diformyl[2.2]paracyclophane as starting material. The title compound may be used as a valuable precursor for the synthesis of diethynyl[2.2]paracyclophane. The title molecule is centrosymmetric with a crystallographic center of inversion between the centers of the two phenyl rings. A strong tilting is observed with an interplanar angle between the best aromatic plane and the vinyl plane of $49.4(5)^\circ$. No significant intermolecular interactions are found in the crystal.

Related literature

For related structures of halovinyl compounds, see: Clément *et al.* (2007*a,b*); Jones *et al.* (1993); Hua *et al.* (2006). For ethynyl-functionalized[2.2]paracyclophanes, see: Jones *et al.* (2007). For the Corey–Fuchs reaction, see: Corey *et al.* (1972). For applications of [2.2]paracyclophanes, see: Hopf *et al.* (2008). For an alternative to the classical Sonogashira synthesis, see: Morisaki *et al.* (2003).



Experimental

Crystal data

$\text{C}_{20}\text{H}_{16}\text{Br}_4$	$V = 1867.9(3) \text{ \AA}^3$
$M_r = 575.97$	$Z = 4$
Orthorhombic, $Pbca$	Mo $K\alpha$ radiation
$a = 12.155(1) \text{ \AA}$	$\mu = 8.62 \text{ mm}^{-1}$
$b = 8.3819(9) \text{ \AA}$	$T = 173(2) \text{ K}$
$c = 18.335(2) \text{ \AA}$	$0.30 \times 0.20 \times 0.10 \text{ mm}$

Data collection

Bruker APEX CCD diffractometer	16030 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 1999)	2043 independent reflections
$T_{\min} = 0.141$, $T_{\max} = 0.418$	1766 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$	109 parameters
$wR(F^2) = 0.073$	H-atom parameters constrained
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.84 \text{ e \AA}^{-3}$
2043 reflections	$\Delta\rho_{\text{min}} = -0.60 \text{ e \AA}^{-3}$

Data collection: SMART (Bruker, 2001); cell refinement: SAINT-Plus (Bruker, 2001); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2094).

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supporting information

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4,12-Bis(2,2-dibromovinyl)[2.2]paracyclophane

Sébastien Clément, Laurent Guyard, Michael Knorr, Christian Däschlein and Carsten Strohmann

S1. Comment

In the context of our research in developing novel π -conjugated functionalized [2.2]paracyclophanes and ferrocenes (Clément *et al.*, 2007a) for potential applications in coordination chemistry, we have recently reported an alternative to the classical Sonogashira synthesis (Morisaki *et al.*, 2003) for the synthesis of ethynyl functionalized [2.2]paracyclophanes (Scheme 2). Our route involves a Corey-Fuchs reaction (Clément *et al.*, 2007b) and subsequent dehydrobromination induced by a strong base. In the first step, an ylide species, formed *in situ* by the interaction of zinc dust, CBr₄ and PPh₃, reacts with the formyl derivative **1a** or **1b** leading to the dibromoolefin derivatives **2a** or **2b**. The molecular structure of the vinylic intermediate **2b** was elucidated by a single-crystal X-ray diffraction study (Figure 1).

2b possesses a crystallographic center of inversion in the middle of the cyclophane framework. Bond lengths and angles may be considered as normal. Distortions typical of [2.2]paracyclophane systems, *e.g.* lengthened C—C bonds and widened angles in the bridges, narrowed ring bond angles at the bridgehead atoms, and boat-like distortion of the rings (the bridgehead atoms lie significantly out of the plane of the other four ring atoms) are observed. As previously noticed for the monodibromoolefin compound **2a**, the alkenyl unit of **2b** is strongly tilted. The two best planes of the arene (C3, C4, C5, C6, C7, C8; plane 1) and the vinyl-group (Br1, Br2, C1, C2; plane 2) possess a cutting angle of the normals of 49.4 (5)°

Contrary to a recently published, related system, no significant intermolecular interactions are observed for **2b** due to improper orientation of the molecules relative to each other (Hopf *et al.*, 2007).

In the light of our recent work on the reactivity of (2,2-dibromovinyl)ferrocene towards thiolates (Clément *et al.*, 2007b), the vinylic intermediates **2a** and **2b** should be promising starting materials for building new ligand systems. Synthesis, reactivity and photochemical properties of these new compounds will be reported in due course.

S2. Experimental

PPh₃ (4.20 g, 16.0 mmol), CBr₄ (5.31 g, 16.0 mmol) and zinc dust (1.05 g, 16.0 mmol) are placed in a Schlenk tube and CH₂Cl₂ (45 ml) is added slowly. The mixture is stirred at room temperature for 28 h. Then, **1b** (1.05 g, 4.00 mmol), dissolved in CH₂Cl₂ (20 ml), is added and stirring is continued for 2 h. The reaction mixture is extracted with three 50 ml portions of pentane. CH₂Cl₂ is added when the reaction mixture became too viscous for further extractions. The extracts are filtered and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel with CH₂Cl₂/petroleum ether (1:1). Slow evaporation afforded white crystals of **2b** (Yield: 94%). mp 183°C, ¹H NMR (CDCl₃): 3.00 (m, 7H, CH₂), 3.24 (m, 1H, CH₂), 6.43 (d, 2H, *J* = 8.2 Hz, H_{aromatic}), 6.59 (d, 2H, *J* = 2.1 Hz, H_{aromatic}), 6.65 (dd, 2H, *J* = 8.2 Hz, *J* = 2.1 Hz, H_{aromatic}), 7.43 (s, 2H, CH=CBr₂) p.p.m.. ¹³C {¹H} NMR (CDCl₃): 34.9, 35.4 (C-1, C-2, C-9, C-10), 90.5 (C-18, C-20), 130.5, 134.0, 135.7, 135.8 (C-5, C-7, C-8, C-12, C-13, C-15, C-16, C-17), 136.2 (C-4, C-16), 138.1, 139.3 (C-3, C-6, C-11, C-14) p.p.m.. UV-vis (CH₂Cl₂)[I_{max} nm (*e*): 229 (57544 M⁻¹.cm⁻¹), 266 (20417 M⁻¹.cm⁻¹).

Anal. Calcd for $C_{20}H_{16}Br_4$: C, 41.71, H, 2.80, Found: C, 41.63, H, 2.71. (Clément *et al.*, 2007b).

S3. Refinement

Refinement was accomplished by full-matrix least-squares methods (based on Fo2, *SHELXL97*); anisotropic thermal parameters for all non-H atoms in the final cycles; hydrogen atoms were placed in calculated positions and refined using a riding model with $U_{iso}(H) = 1.2 U_{eq}(C)$.

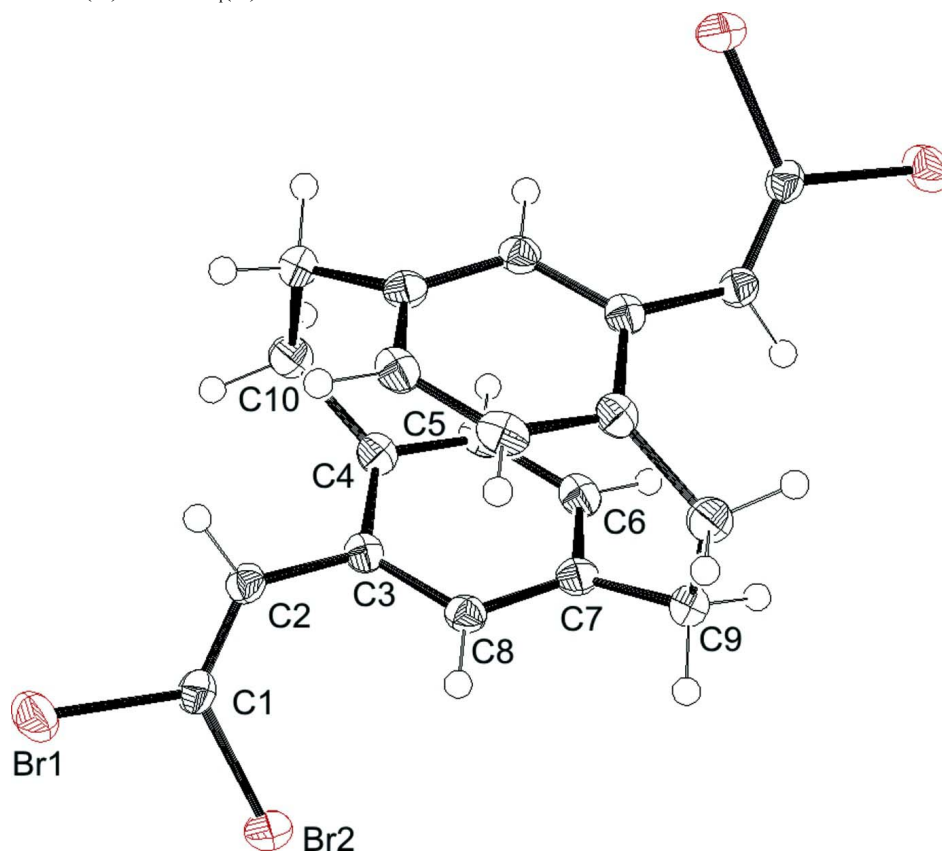


Figure 1

ORTEP plot of **2b** with 30% probability level.

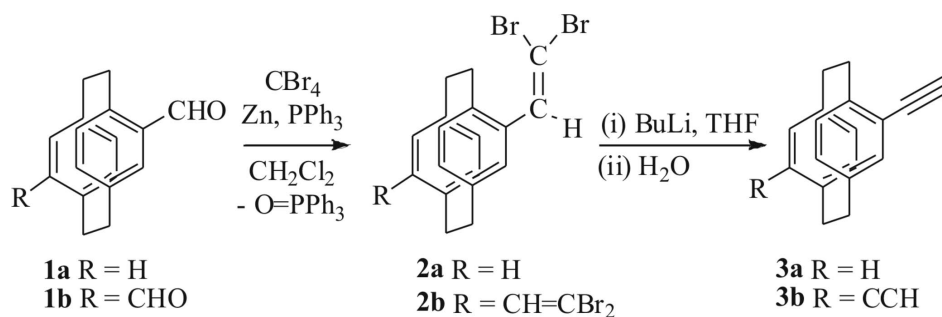


Figure 2

The formation of the title compound.

4,12-Bis(2,2-dibromovinyl)[2.2]paracyclophane*Crystal data*C₂₀H₁₆Br₄ $M_r = 575.97$ Orthorhombic, *Pbca*

Hall symbol: -P 2ac 2ab

 $a = 12.155 (1) \text{ \AA}$ $b = 8.3819 (9) \text{ \AA}$ $c = 18.335 (2) \text{ \AA}$ $V = 1867.9 (3) \text{ \AA}^3$ $Z = 4$ $F(000) = 1104$ $D_x = 2.048 \text{ Mg m}^{-3}$

Melting point: 456 K

Mo *K* α radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1766 reflections

 $\theta = 2.2\text{--}27.0^\circ$ $\mu = 8.62 \text{ mm}^{-1}$ $T = 173 \text{ K}$

Irregular, white

 $0.30 \times 0.20 \times 0.10 \text{ mm}$ *Data collection*

Bruker APEX CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

CCD scans

Absorption correction: multi-scan

(SADABS; Bruker, 1999)

 $T_{\min} = 0.141, T_{\max} = 0.418$

16030 measured reflections

2043 independent reflections

1766 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.045$ $\theta_{\text{max}} = 27.0^\circ, \theta_{\text{min}} = 2.2^\circ$ $h = -15 \rightarrow 15$ $k = -10 \rightarrow 10$ $l = -23 \rightarrow 23$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.032$ $wR(F^2) = 0.073$ $S = 1.08$

2043 reflections

109 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-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0298P)^2 + 3.2824P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} = 0.001$ $\Delta\rho_{\text{max}} = 0.84 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.60 \text{ e \AA}^{-3}$ *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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.94392 (3)	0.12568 (5)	0.72066 (2)	0.03823 (13)
Br2	1.18942 (3)	0.01277 (4)	0.70021 (2)	0.03403 (12)
C1	1.0695 (3)	0.1284 (4)	0.66105 (19)	0.0223 (7)
C2	1.0750 (3)	0.1954 (4)	0.59555 (18)	0.0216 (7)

H2	1.1423	0.1819	0.5699	0.026*
C3	0.9893 (3)	0.2882 (4)	0.55781 (18)	0.0198 (6)
C4	0.9745 (3)	0.2705 (4)	0.48219 (18)	0.0215 (7)
C5	0.8859 (3)	0.3511 (4)	0.45039 (19)	0.0250 (7)
H5	0.8626	0.3226	0.4027	0.030*
C6	0.8316 (3)	0.4717 (4)	0.4873 (2)	0.0241 (7)
H6	0.7720	0.5255	0.4645	0.029*
C7	0.8632 (3)	0.5151 (4)	0.55752 (19)	0.0227 (7)
C8	0.9336 (3)	0.4115 (4)	0.59427 (18)	0.0213 (7)
H8	0.9442	0.4246	0.6453	0.026*
C9	0.8418 (3)	0.6819 (4)	0.5856 (2)	0.0280 (8)
H9A	0.8312	0.6778	0.6391	0.034*
H9B	0.7729	0.7228	0.5636	0.034*
C10	1.0610 (3)	0.1987 (4)	0.43258 (19)	0.0263 (7)
H10A	1.0256	0.1650	0.3864	0.032*
H10B	1.0918	0.1023	0.4562	0.032*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0365 (2)	0.0460 (2)	0.0321 (2)	0.01147 (17)	0.01440 (17)	0.01208 (17)
Br2	0.0273 (2)	0.0414 (2)	0.0335 (2)	0.00426 (16)	-0.00318 (15)	0.01310 (16)
C1	0.0172 (15)	0.0229 (15)	0.0267 (17)	0.0017 (13)	-0.0003 (13)	-0.0005 (13)
C2	0.0174 (15)	0.0218 (15)	0.0256 (17)	0.0000 (12)	0.0026 (13)	0.0015 (13)
C3	0.0163 (15)	0.0181 (15)	0.0251 (17)	-0.0045 (12)	0.0000 (13)	0.0023 (12)
C4	0.0238 (17)	0.0148 (14)	0.0260 (17)	-0.0054 (12)	-0.0006 (13)	-0.0006 (12)
C5	0.0257 (17)	0.0270 (17)	0.0223 (18)	-0.0090 (14)	-0.0035 (14)	0.0024 (13)
C6	0.0173 (16)	0.0240 (16)	0.0309 (19)	-0.0051 (13)	-0.0015 (14)	0.0065 (14)
C7	0.0182 (16)	0.0245 (16)	0.0254 (18)	-0.0033 (13)	0.0047 (13)	0.0034 (13)
C8	0.0198 (16)	0.0228 (16)	0.0212 (16)	-0.0022 (13)	0.0011 (13)	0.0024 (12)
C9	0.0298 (18)	0.0275 (17)	0.0266 (19)	0.0080 (14)	0.0060 (15)	0.0040 (14)
C10	0.0342 (19)	0.0224 (15)	0.0223 (17)	-0.0003 (14)	-0.0004 (15)	-0.0027 (13)

Geometric parameters (Å, °)

Br1—C1	1.878 (3)	C6—C7	1.392 (5)
Br2—C1	1.892 (3)	C6—H6	0.9500
C1—C2	1.328 (5)	C7—C8	1.392 (4)
C2—C3	1.473 (4)	C7—C9	1.512 (5)
C2—H2	0.9500	C8—H8	0.9500
C3—C8	1.405 (4)	C9—C10 ⁱ	1.584 (5)
C3—C4	1.406 (5)	C9—H9A	0.9900
C4—C5	1.399 (5)	C9—H9B	0.9900
C4—C10	1.515 (5)	C10—C9 ⁱ	1.584 (5)
C5—C6	1.385 (5)	C10—H10A	0.9900
C5—H5	0.9500	C10—H10B	0.9900
C2—C1—Br1	124.9 (2)	C6—C7—C8	117.0 (3)

C2—C1—Br2	121.4 (2)	C6—C7—C9	120.5 (3)
Br1—C1—Br2	113.53 (17)	C8—C7—C9	121.2 (3)
C1—C2—C3	127.8 (3)	C7—C8—C3	121.6 (3)
C1—C2—H2	116.1	C7—C8—H8	119.2
C3—C2—H2	116.1	C3—C8—H8	119.2
C8—C3—C4	119.0 (3)	C7—C9—C10 ⁱ	112.6 (3)
C8—C3—C2	120.4 (3)	C7—C9—H9A	109.1
C4—C3—C2	119.9 (3)	C10 ⁱ —C9—H9A	109.1
C5—C4—C3	117.3 (3)	C7—C9—H9B	109.1
C5—C4—C10	118.4 (3)	C10 ⁱ —C9—H9B	109.1
C3—C4—C10	123.0 (3)	H9A—C9—H9B	107.8
C6—C5—C4	121.1 (3)	C4—C10—C9 ⁱ	113.1 (3)
C6—C5—H5	119.5	C4—C10—H10A	109.0
C4—C5—H5	119.5	C9 ⁱ —C10—H10A	109.0
C5—C6—C7	120.7 (3)	C4—C10—H10B	109.0
C5—C6—H6	119.6	C9 ⁱ —C10—H10B	109.0
C7—C6—H6	119.6	H10A—C10—H10B	107.8

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