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A tetrabromo-1,4-ethanonaphthalene and related dibromo-1,4-ethenonaphthalene

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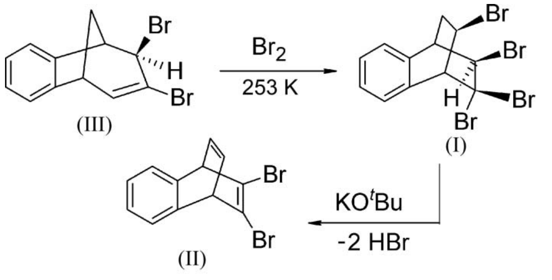
(1*RS*,3*RS*,4*RS*,10*SR*)-2,2,3,10-Tetrabromo-1,2,3,4-tetrahydro-1,4-ethanonaphthalene, $C_{12}H_{10}Br_4$, (I), is the first structure to be reported with four Br atoms bound to a 1,4-ethanonaphthalene framework and also the first which possesses three Br atoms in *exo* positions. Interactions between the Br atoms [three short intramolecular Br$\cdots$Br distances of 3.1094 (4), 3.2669 (4) and 3.4415 (5) Å] have little effect on the C—C bond lengths but lead to significant twisting of the cage structure compared with the parent hydrocarbon, which is expected to be fully eclipsed at the two saturated C_2H_4 bridge positions. Chemically related (1*SR*,4*RS*)-2,3-dibromo-1,4-ethenonaphthalene, $C_{12}H_8Br_2$, (II), obtained by double dehydrobromination of (I), represents the first structure of any halogen-substituted benzobarrelene. This *cis*-dibromide shows little evidence of steric congestion at the double bond [Br$\cdots$Br = 3.5276 (8) Å] as a consequence of the large C—C—Br angles [average C═C—Br angle = 126.15 (10)°].

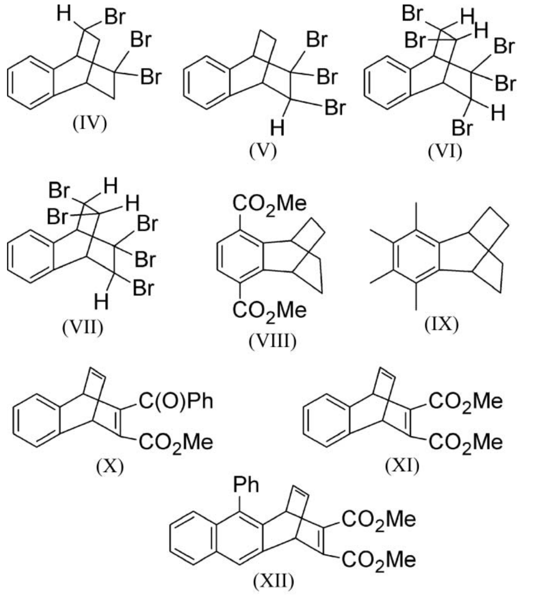
Comment

We recently reported the crystal and molecular structure of the useful intermediate 3,4-dibromo-6,7-benzobicyclo[3.2.1]-octa-2,6-diene, (III) (Johnson *et al.*, 2011) (Scheme 1). We report here on two related structures which provide access to a variety of substituted benzobarrelenes (Çakmak & Balcı, 1989; Bender *et al.*, 2003). Compound (I) (Fig. 1) is formed by the addition of bromine to (III) and is the direct precursor, by double dehydrobromination, of the extremely useful 2,3-dibromo-1,4-ethenonaphthalene (II) (Fig. 2). We have used (II), *inter alia*, in the preparation of specifically labelled deuterated species such as 2-bromo-3-deuterobenzobarrelene (Bender *et al.*, 2003).



Scheme 1

The crystal structure of tetrabromo-1,2,3,4-tetrahydro-1,4-ethanonaphthalene, (I), is the first reported for any tetrabromo derivative of the 1,2,3,4-tetrahydro-1,4-ethanonaphthalene framework. Structures are known for two tribromides, *viz.* (1*RS*,4*SR*,10*SR*)-2,2,10-tribromo-1,2,3,4-tetrahydro-1,4-ethanonaphthalene, (IV) [Cambridge Structural Database (CSD; Allen, 2002) refcode FOMREE (Ergin *et al.*, 1987)] (Scheme 2) and (1*RS*,3*SR*,4*SR*)-2,2,3-tribromo-1,2,3,4-tetrahydro-1,4-ethanonaphthalene, (V) (refcode KAKVEZ; Eşsiz *et al.*, 2011). Thus, (IV) lacks the Br atom at position 3, whilst (V) lacks that at position 10 compared with (I). Note that both of the variable Br-atom locations are in the *exo* position.



Scheme 2

There are two reported structures for pentabromide isomers, *viz.* (1*SR*,3*RS*,4*RS*,9*SR*,10*RS*)-2,2,3,9,10-pentabromo-1,2,3,4-tetrahydro-1,4-ethanonaphthalene, (VI) (refcode MOCWUW; Ülkü *et al.*, 2002) and (1*SR*,3*SR*,4*RS*,9*SR*,10*RS*)-2,2,3,9,10-pentabromo-1,2,3,4-tetrahydro-1,4-ethanonaphthalene, (VII) (refcode TAFXIH; Hökelek *et al.*, 1990). The latter two differ, respectively, in the *endo versus exo* orientation of the Br atom at position 3. The geometry of the parent hydrocarbon framework without substituents on the bicyclic cage is available in 5,8-diacetoxy-1,2,3,4-tetrahydro-1,4-ethanonaphthalene, (VIII) (refcode EDAGUM; Goh *et al.*, 2007), and in the structure of a cocrystal of 5,6,7,8-tetramethyl-1,2,3,4-tetrahydro-1,4-ethanonaphthalene, (IX) (refcode PAWDIA; Rathore *et al.*, 1998). In (IV)–(IX), the two single bonds attached to benzene [equivalent to C1—C2 and C7—C8 in (I)] average 1.505 (9) Å, a value not statistically different from the average value in (I) of 1.517 (6) Å. However, these bonds appear shorter than the remaining cage bonds at the

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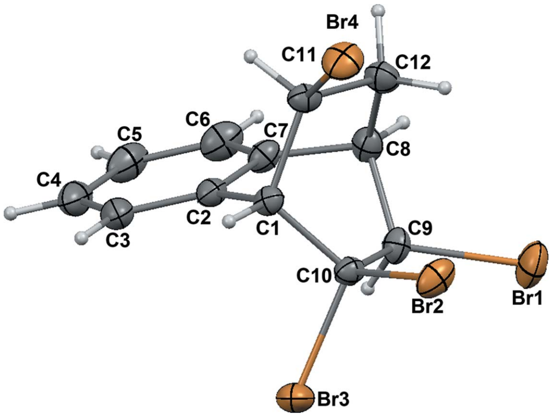

Figure 1
The molecular structure of (I), showing the atom-numbering scheme, with displacement ellipsoids drawn at the 50% probability level. The crystal is a racemate; the displayed molecule has the following stereochemical centres: C1 *R*, C8 *R*, C9 *R* and C11 *S*.

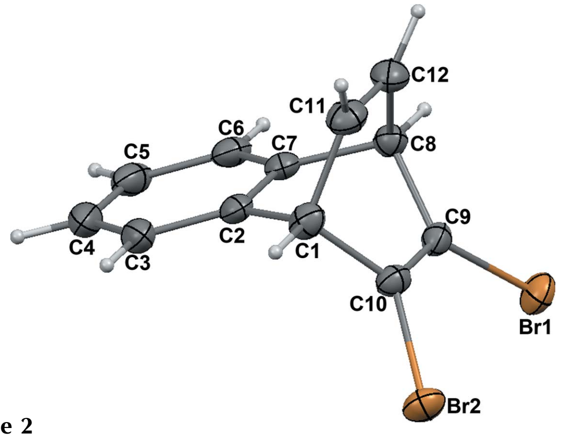

Figure 2
The molecular structure of (II), showing the atom-numbering scheme, with displacement ellipsoids drawn at the 50% probability level. The displayed molecule has the following stereochemical centres: C1 *S* and C8 *R*.

95% confidence level; the latter have a mean value in (IV)–(IX) of 1.544 (10) Å, once the lowest outliers in Fig. 3 have been omitted. The mean value for these bonds in (I) of 1.545 (5) Å represents a very good match. Over all seven structures, there appears to be a slight trend towards longer C—C distances for those bonds substituted with two Br atoms at one end and one Br atom at the other, which average 1.558 (9) Å, but the difference from the distribution shown in Fig. 3 is not statistically significant for this sample.

If the conformation around the boat cyclohexane ring (atoms C1, C10, C9, C8, C12 and C11) is considered, (I) is the most distorted of this comparison set from the essentially pure boat conformations observed in (VIII) and (XI) [even though (VI) and (VII) are pentabromides]. This may be a consequence of its being the only example with three *exo* Br atoms, arranged in a 1,2,4 all-axial substitution pattern around this saturated six-membered ring. Thus, the torsion angles at the ethane bridges of 18.8 (2) (Br1—C9—C10—Br2) and 35.3 (2)° (Br4—C11—C12—H12*A*) in (I) are considerably larger than in the comparison set. Visually, this ring is also distorted in (IV). A Cremer & Pople conformational analysis (Cremer & Pople, 1975) for (I), undertaken using *PLATON* (Spek, 2009), results in puckering parameters of Q = 0.829 (3) Å, θ = 92.8 (2)° and φ = 19.24 (19)° for the C1/C10/C9/C8/C12/C11 ring, whereas for (IV), Q = 0.823 (16) Å, θ = 94.3 (11)° and φ = 7.4 (11)° for the analogous ring. Thus, the conformation in (I) is intermediate but closer to the twist-boat limit (φ = 0° for boat and 30° for twisted), whereas that in (IV) is much closer to a boat conformation.

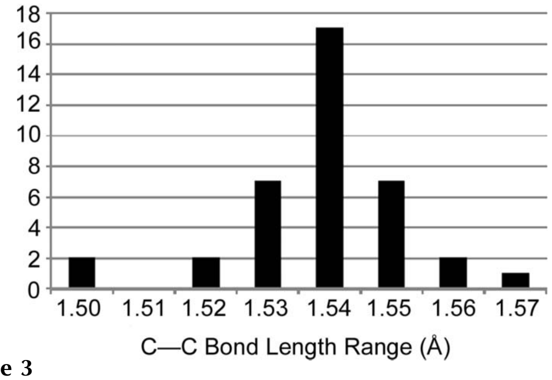

Figure 3
The bond-length distribution for cage C—C bonds other than those attached to benzene rings in (IV)–(IX). The corresponding mean value in (I) is 1.545 (5) Å.

The molecules of (I) lack any symmetry and stack along the *a* axis of the unit cell, with short Br3···C4^{ii} contacts of 3.430 (3) Å. However, the strongest interaction is probably between atom Br3 and the benzene ring centroid [3.332 (3) Å] (see Fig. 4 for symmetry code).

To date, no crystal structures have been reported for any derivatives of a mono-fused bicyclo[2.2.2]octa-1(7),4(8),5-triene (*i.e.* a benzobarrelene) bearing halogen substituents on the framework atoms. Indeed, a search of the CSD (WebCSD, December 2012) returned only seven structures for this class of compound (excluding metal complexes). Of these, the examples with electron-withdrawing substituents that might be most comparable with (II) are methyl 2-benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate, (X) (refcode

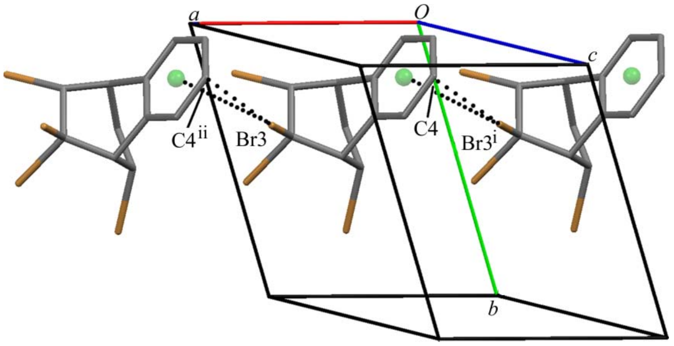

Figure 4
Short intermolecular Br3···C4 and Br3···benzene ring centroid contacts linking the molecules of (I) in a straight chain parallel to the crystallographic *a* axis. Ring centroids are indicated by large spheres and dotted lines denote the interactions. [Symmetry codes: (i) $x - 1, y, z$; (ii) $x + 1, y, z$.]

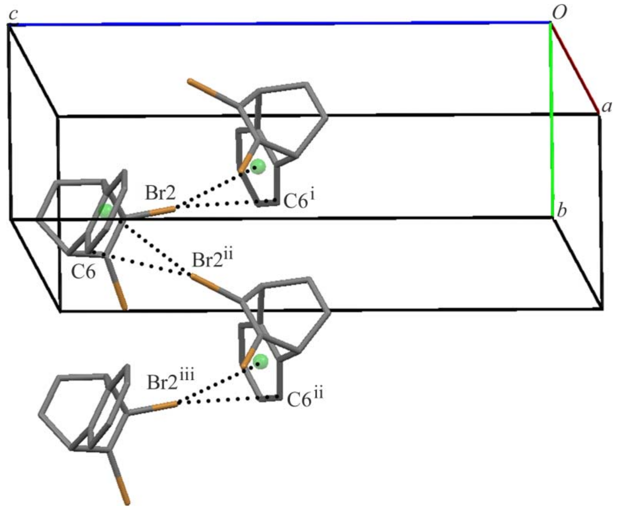

Figure 5
Short intermolecular Br2···C6 and Br2···benzene ring centroid contacts linking the molecules of (II) in a zigzag chain parallel to the crystallographic *a* axis. Ring centroids are indicated by large spheres and dotted lines denote the interactions. [Symmetry codes: (i) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x, y+1, z$.]

LEKLAO; Pokkuluri, Scheffer, Trotter & Yap, 1994), dimethyl 7,8-benzobicyclo[2.2.2]octa-2,5,7-triene-2,3-dicarboxylate, (XI) (refcode SATPUY; Trotter, 1989), and dimethyl 9-phenyl-1,4-dihydro-1,4-ethenoanthracene-11,12-dicarboxylate, (XII) (refcode WEJBOC; Pokkuluri, Scheffer, & Trotter, 1994). In this sample of four structures, the single bonds of the barrelenes are indistinguishable, with an average length of 1.526 (9) Å. Interestingly, for the nonfused C=C bonds, those in (II) fit best with the 'unsubstituted' analogues, at an average distance of 1.315 (4) Å, whereas the C=C bonds bearing the ester or ketone substituents in (X)–(XII) are longer, with an average of 1.337 (6) Å, suggesting that in these cases there is steric congestion resulting from the 1,2-substitution of the carbonyl groups. And yet the Br atoms in (II) seem to cause little crowding; the intramolecular Br1···Br2 contact distance is 3.5276 (8) Å, only marginally less than the sums of their van der Waals radii (Bondi, 1964). Whilst it is true that the C10—C9—Br1 [126.50 (14)°] and C9—C10—Br2 [125.79 (14)°] angles are wide, this is just as likely to be a consequence of the pinching of the interior angles at atoms C9 and C10 by the bicyclic cage geometry as it is to be due to steric pressure between the Br atoms.

Molecules of (II) possess noncrystallographic point symmetry *m*. Short intermolecular Br2···C6^{i} contacts [3.512 (2) Å] link them into a zigzag chain parallel to the crystallographic *b* axis (see Fig. 5 for symmetry code). Here too, just as in (I), the strongest interaction is between Br and neighbouring benzene ring centroids, at 3.480 (3) Å.

Experimental

Tetrabromide (I) was readily prepared by the addition of bromine to (III) at 253 K, accompanied by a rearrangement of the hydrocarbon cage, as shown in Scheme 1 (Kitahonoki *et al.*, 1969; Johnson *et al.*, 2011). Recrystallization of the reaction mixture from chloroform–hexane (1:1 *v*/*v*) gave colourless block-shaped crystals of (I) (yield 54%, m.p. 418–419 K). Dibromide (II) was prepared by the double dehydrobromination of (I), according to the method of Çakmak & Balcı (1989) (yield >80%, m.p. 344–345 K), and was recrystallized from dichloromethane–pentane (1:2 *v*/*v*).

Compound (I)

Crystal data

$C_{12}H_{10}Br_4$
$M_r = 473.84$
Triclinic, $P\overline{1}$
$a = 6.9532$ (4) Å
$b = 8.4323$ (5) Å
$c = 11.9669$ (7) Å
$\alpha = 94.706$ (1)°
$\beta = 91.257$ (1)°
$\gamma = 110.892$ (1)°
$V = 652.31$ (7) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 12.31$ mm^{-1}
$T = 173$ K
0.45 × 0.27 × 0.27 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: numerical (*SADABS*; Bruker, 2008)
$T_{\min} = 0.052$, $T_{\max} = 0.144$
7682 measured reflections
3074 independent reflections
2835 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.055$
$S = 1.05$
3074 reflections
146 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.78$ e Å^{-3}
$\Delta\rho_{\min} = -0.78$ e Å^{-3}

Compound (II)

Crystal data

$C_{12}H_8Br_2$
$M_r = 312.00$
Monoclinic, $P2_1/n$
$a = 9.520$ (3) Å
$b = 6.5032$ (18) Å
$c = 17.124$ (5) Å
$\beta = 100.826$ (3)°
$V = 1041.3$ (5) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 7.74$ mm^{-1}
$T = 173$ K
0.21 × 0.16 × 0.15 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{\min} = 0.291$, $T_{\max} = 0.384$
14301 measured reflections
2378 independent reflections
2076 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.049$
$S = 1.03$
2378 reflections
128 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.51$ e Å^{-3}
$\Delta\rho_{\min} = -0.35$ e Å^{-3}

C-bound H atoms were treated as riding, with C—H = 0.99 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ for methylene, C—H = 1.00 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ for methine, and C—H = 0.95 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ for vinyl and aromatic H atoms. No data were rejected for (I), but three intense reflections and one inconsistent equivalent in the data set of (II) were omitted from the refinement. The largest peak and deepest hole in the final difference maps approach the equivalent electron density of an H atom but are located less than 1 Å from Br atoms.

For both compounds, data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT-Plus* (Bruker, 2008); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Dr Douglas Dolman and Sherry Lawson (University of Lethbridge) are thanked for sample preparation. Ben J. Ireland and Mohammed R. Hassan assisted with the data collection as part of instrument training. This research was supported by the Natural Sciences and Engineering Research Council of Canada. The diffractometer at the University of Lethbridge X-ray Diffraction Facility was purchased with the help of NSERC and the University.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3227). Services for accessing these data are described at the back of the journal.

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supplementary materials

Acta Cryst. (2013). C**69**, 247-250   [doi:10.1107/S010827011300231X]

A tetrabromo-1,4-ethanonaphthalene and related dibromo-1,4-etheno-naphthalene

René T. Boeré and Christopher O. Bender

(I) (1*RS*,3*RS*,4*RS*,10*SR*)-2,2,3,10-Tetrabromo-1,2,3,4-tetrahydro-1,4-ethanonaphthalene

Crystal data

$C_{12}H_{10}Br_4$
M_r = 473.84
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 6.9532 (4) Å
b = 8.4323 (5) Å
c = 11.9669 (7) Å
α = 94.706 (1)°
β = 91.257 (1)°
γ = 110.892 (1)°
V = 652.31 (7) Å^3

Z = 2
$F(000)$ = 444
D_x = 2.412 Mg m^{-3}
Melting point: 418 K
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6183 reflections
θ = 2.6–28.3°
μ = 12.31 mm^{-1}
T = 173 K
Block, colourless
0.45 × 0.27 × 0.27 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube, Bruker D8
Graphite monochromator
Detector resolution: 66.06 pixels mm^{-1}
φ and ω scans
Absorption correction: numerical (*SADABS*; Bruker, 2008)

T_{min} = 0.052, T_{max} = 0.144
7682 measured reflections
3074 independent reflections
2835 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 28.3°, θ_{min} = 1.7°
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 11$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.055
S = 1.05
3074 reflections
146 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
$w = 1/[\sigma^2(F_o^2) + (0.0202P)^2 + 0.8639P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.78 e Å^{-3}
$\Delta\rho_{min}$ = −0.77 e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0097 (6)

Special details

Experimental. A crystal coated in Paratone (TM) oil was mounted on the end of a thin glass capillary and cooled in the gas stream of the diffractometer Kryoflex device. On consideration of the large absorption coefficient, a face-indexed numerical absorption correction was undertaken using *SADABS* software.

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 (Å²)

	x	y	z	$U_{\text{iso}}*/U_{\text{eq}}$
Br1	0.89779 (5)	0.17616 (4)	0.04487 (2)	0.03611 (9)
Br2	1.08266 (4)	0.55118 (3)	0.18715 (2)	0.02900 (8)
Br3	1.03300 (4)	0.31408 (4)	0.37875 (2)	0.02923 (8)
Br4	0.70724 (4)	0.72876 (3)	0.18717 (2)	0.03075 (9)
C1	0.7185 (3)	0.4386 (3)	0.3143 (2)	0.0182 (4)
H1	0.7836	0.5321	0.3756	0.022*
C2	0.5540 (4)	0.2863 (3)	0.3576 (2)	0.0199 (5)
C3	0.4997 (4)	0.2671 (3)	0.4675 (2)	0.0249 (5)
H3	0.5704	0.3528	0.5260	0.030*
C4	0.3393 (4)	0.1196 (4)	0.4913 (2)	0.0313 (6)
H4	0.3012	0.1047	0.5666	0.038*
C5	0.2358 (4)	−0.0045 (4)	0.4063 (3)	0.0327 (6)
H5	0.1265	−0.1038	0.4235	0.039*
C6	0.2899 (4)	0.0143 (3)	0.2960 (3)	0.0300 (6)
H6	0.2184	−0.0716	0.2378	0.036*
C7	0.4492 (4)	0.1597 (3)	0.2715 (2)	0.0220 (5)
C8	0.5393 (4)	0.1937 (3)	0.1582 (2)	0.0223 (5)
H8	0.4660	0.0973	0.1001	0.027*
C9	0.7635 (4)	0.2064 (3)	0.1817 (2)	0.0214 (5)
H9	0.7562	0.1092	0.2261	0.026*
C10	0.8784 (3)	0.3726 (3)	0.2598 (2)	0.0188 (4)
C11	0.5907 (4)	0.4919 (3)	0.2267 (2)	0.0202 (5)
H11	0.4572	0.4802	0.2612	0.024*
C12	0.5356 (4)	0.3639 (3)	0.1222 (2)	0.0248 (5)
H12A	0.6367	0.4055	0.0645	0.030*
H12B	0.3969	0.3484	0.0902	0.030*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.03552 (16)	0.04056 (17)	0.03069 (16)	0.01369 (13)	0.01088 (11)	−0.00776 (11)
Br2	0.02253 (13)	0.02120 (13)	0.04350 (17)	0.00627 (10)	0.01178 (11)	0.00922 (10)
Br3	0.02532 (14)	0.03823 (16)	0.02935 (15)	0.01712 (11)	−0.00090 (10)	0.00695 (11)
Br4	0.03562 (16)	0.02153 (13)	0.03915 (16)	0.01381 (11)	0.00586 (11)	0.00839 (10)

C1	0.0176 (10)	0.0165 (10)	0.0201 (11)	0.0063 (9)	−0.0001 (8)	−0.0004 (8)
C2	0.0174 (11)	0.0204 (11)	0.0232 (12)	0.0081 (9)	0.0031 (9)	0.0037 (9)
C3	0.0258 (12)	0.0301 (13)	0.0229 (12)	0.0147 (11)	0.0020 (10)	0.0031 (10)
C4	0.0290 (13)	0.0399 (15)	0.0321 (14)	0.0175 (12)	0.0108 (11)	0.0179 (12)
C5	0.0255 (13)	0.0269 (13)	0.0485 (17)	0.0094 (11)	0.0132 (12)	0.0166 (12)
C6	0.0233 (12)	0.0203 (12)	0.0433 (16)	0.0039 (10)	0.0042 (11)	0.0034 (11)
C7	0.0192 (11)	0.0187 (11)	0.0276 (13)	0.0061 (9)	0.0042 (9)	0.0020 (9)
C8	0.0206 (11)	0.0212 (11)	0.0215 (12)	0.0041 (9)	0.0006 (9)	−0.0030 (9)
C9	0.0242 (12)	0.0189 (11)	0.0211 (11)	0.0077 (9)	0.0054 (9)	0.0003 (9)
C10	0.0157 (10)	0.0196 (11)	0.0210 (11)	0.0061 (9)	0.0018 (8)	0.0032 (9)
C11	0.0176 (11)	0.0187 (11)	0.0243 (12)	0.0062 (9)	0.0001 (9)	0.0034 (9)
C12	0.0227 (12)	0.0280 (13)	0.0224 (12)	0.0080 (10)	−0.0030 (9)	0.0010 (10)

Geometric parameters (Å, º)

Br1—C9	1.946 (2)	C5—C6	1.386 (4)
Br2—C10	1.945 (2)	C5—H5	0.9500
Br3—C10	1.963 (2)	C6—C7	1.386 (4)
Br4—C11	1.972 (2)	C6—H6	0.9500
C1—C2	1.521 (3)	C7—C8	1.512 (3)
C1—C10	1.544 (3)	C8—C12	1.540 (4)
C1—C11	1.553 (3)	C8—C9	1.542 (3)
C1—H1	1.0000	C8—H8	1.0000
C2—C3	1.383 (3)	C9—C10	1.558 (3)
C2—C7	1.401 (3)	C9—H9	1.0000
C3—C4	1.398 (4)	C11—C12	1.529 (3)
C3—H3	0.9500	C11—H11	1.0000
C4—C5	1.380 (4)	C12—H12A	0.9900
C4—H4	0.9500	C12—H12B	0.9900
C2—C1—C10	106.98 (18)	C7—C8—H8	111.1
C2—C1—C11	101.56 (18)	C12—C8—H8	111.1
C10—C1—C11	112.57 (19)	C9—C8—H8	111.1
C2—C1—H1	111.7	C8—C9—C10	108.73 (19)
C10—C1—H1	111.7	C8—C9—Br1	112.40 (16)
C11—C1—H1	111.7	C10—C9—Br1	115.76 (16)
C3—C2—C7	120.3 (2)	C8—C9—H9	106.4
C3—C2—C1	127.0 (2)	C10—C9—H9	106.4
C7—C2—C1	112.6 (2)	Br1—C9—H9	106.4
C2—C3—C4	119.0 (2)	C1—C10—C9	109.21 (19)
C2—C3—H3	120.5	C1—C10—Br2	110.96 (16)
C4—C3—H3	120.5	C9—C10—Br2	114.66 (16)
C5—C4—C3	120.5 (3)	C1—C10—Br3	108.67 (16)
C5—C4—H4	119.8	C9—C10—Br3	107.65 (16)
C3—C4—H4	119.8	Br2—C10—Br3	105.43 (11)
C4—C5—C6	120.7 (3)	C12—C11—C1	109.83 (19)
C4—C5—H5	119.7	C12—C11—Br4	111.59 (16)
C6—C5—H5	119.7	C1—C11—Br4	116.66 (16)
C7—C6—C5	119.4 (3)	C12—C11—H11	106.0
C7—C6—H6	120.3	C1—C11—H11	106.0

C5—C6—H6	120.3	Br4—C11—H11	106.0
C6—C7—C2	120.1 (2)	C11—C12—C8	107.5 (2)
C6—C7—C8	126.1 (2)	C11—C12—H12A	110.2
C2—C7—C8	113.5 (2)	C8—C12—H12A	110.2
C7—C8—C12	111.0 (2)	C11—C12—H12B	110.2
C7—C8—C9	102.1 (2)	C8—C12—H12B	110.2
C12—C8—C9	110.2 (2)	H12A—C12—H12B	108.5

C10—C1—C2—C3	119.7 (3)	C12—C8—C9—Br1	−80.7 (2)
C11—C1—C2—C3	−122.1 (3)	C2—C1—C10—C9	46.8 (2)
C10—C1—C2—C7	−62.3 (3)	C11—C1—C10—C9	−64.0 (2)
C11—C1—C2—C7	55.9 (2)	C2—C1—C10—Br2	174.12 (15)
C7—C2—C3—C4	0.1 (4)	C11—C1—C10—Br2	63.4 (2)
C1—C2—C3—C4	178.0 (2)	C2—C1—C10—Br3	−70.40 (19)
C2—C3—C4—C5	−0.4 (4)	C11—C1—C10—Br3	178.88 (15)
C3—C4—C5—C6	0.4 (4)	C8—C9—C10—C1	16.4 (3)
C4—C5—C6—C7	−0.2 (4)	Br1—C9—C10—C1	144.07 (17)
C5—C6—C7—C2	−0.1 (4)	C8—C9—C10—Br2	−108.78 (19)
C5—C6—C7—C8	174.5 (3)	Br1—C9—C10—Br2	18.8 (2)
C3—C2—C7—C6	0.1 (4)	C8—C9—C10—Br3	134.26 (17)
C1—C2—C7—C6	−178.0 (2)	Br1—C9—C10—Br3	−98.12 (16)
C3—C2—C7—C8	−175.1 (2)	C2—C1—C11—C12	−73.6 (2)
C1—C2—C7—C8	6.7 (3)	C10—C1—C11—C12	40.5 (3)
C6—C7—C8—C12	125.7 (3)	C2—C1—C11—Br4	158.19 (16)
C2—C7—C8—C12	−59.5 (3)	C10—C1—C11—Br4	−87.7 (2)
C6—C7—C8—C9	−116.9 (3)	C1—C11—C12—C8	24.5 (3)
C2—C7—C8—C9	58.0 (3)	Br4—C11—C12—C8	155.47 (16)
C7—C8—C9—C10	−69.2 (2)	C7—C8—C12—C11	39.3 (3)
C12—C8—C9—C10	48.8 (3)	C9—C8—C12—C11	−73.1 (2)
C7—C8—C9—Br1	161.26 (16)		

(II) (1*SR*,4*RS*)-2,3-dibromo-1,4-ethenonaphthalene

Crystal data

$C_{12}H_8Br_2$
$M_r = 312.00$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 9.520$ (3) Å
$b = 6.5032$ (18) Å
$c = 17.124$ (5) Å
$\beta = 100.826$ (3)°
$V = 1041.3$ (5) Å^3
$Z = 4$

$F(000) = 600$
$D_x = 1.990$ Mg m^{-3}
Melting point: 344 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 8250 reflections
$\theta = 2.3$–28.7°
$\mu = 7.74$ mm^{-1}
$T = 173$ K
Block, colourless
0.21 × 0.16 × 0.15 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube, Bruker D8
Graphite monochromator
Detector resolution: 66.06 pixels mm^{-1}

φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min} = 0.291$, $T_{max} = 0.384$
14301 measured reflections
2378 independent reflections

2076 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.029$
$\theta_{\text{max}} = 27.5°$, $\theta_{\text{min}} = 2.3°$
$h = -12 \rightarrow 12$
$k = -8 \rightarrow 8$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.049$
$S = 1.03$
2378 reflections
128 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
$w = 1/[\sigma^2(F_o^2) + (0.0201P)^2 + 0.702P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} = 0.002$
$\Delta\rho_{\text{max}} = 0.51$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.34$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0122 (5)

Special details

Experimental. A crystal coated in Paratone (TM) oil was mounted on the end of a thin glass capillary and cooled in the gas stream of the diffractometer Kryoflex device.

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.95694 (2)	1.00116 (3)	0.877281 (12)	0.03051 (8)
Br2	0.91366 (2)	0.51805 (3)	0.782113 (12)	0.02895 (8)
C1	0.7083 (2)	0.4723 (3)	0.89091 (11)	0.0248 (4)
H1	0.6971	0.3347	0.8644	0.030*
C2	0.57169 (19)	0.6026 (3)	0.87439 (10)	0.0228 (4)
C3	0.4419 (2)	0.5494 (3)	0.82843 (12)	0.0299 (4)
H3	0.4291	0.4189	0.8032	0.036*
C4	0.3293 (2)	0.6909 (4)	0.81956 (12)	0.0355 (5)
H4	0.2387	0.6550	0.7891	0.043*
C5	0.3489 (2)	0.8822 (4)	0.85474 (11)	0.0329 (5)
H5	0.2721	0.9779	0.8473	0.039*
C6	0.4807 (2)	0.9370 (3)	0.90125 (11)	0.0268 (4)
H6	0.4944	1.0689	0.9253	0.032*
C7	0.59055 (19)	0.7949 (3)	0.91135 (10)	0.0216 (4)
C8	0.74157 (19)	0.8223 (3)	0.95989 (10)	0.0222 (4)
H8	0.7566	0.9586	0.9872	0.027*
C9	0.83973 (18)	0.7872 (3)	0.89981 (11)	0.0217 (4)
C10	0.82213 (18)	0.6069 (3)	0.86406 (11)	0.0222 (4)
C11	0.7486 (2)	0.4593 (3)	0.98174 (12)	0.0287 (4)

H11	0.7602	0.3326	1.0098	0.034*
C12	0.7658 (2)	0.6398 (3)	1.01740 (11)	0.0279 (4)
H12	0.7908	0.6551	1.0735	0.033*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02660 (12)	0.02868 (12)	0.03774 (13)	−0.00821 (7)	0.00988 (9)	0.00147 (8)
Br2	0.03114 (12)	0.03011 (12)	0.02878 (12)	0.00309 (7)	0.01384 (8)	−0.00166 (7)
C1	0.0276 (9)	0.0201 (8)	0.0284 (10)	−0.0030 (7)	0.0098 (8)	−0.0022 (7)
C2	0.0233 (9)	0.0277 (9)	0.0196 (8)	−0.0045 (7)	0.0095 (7)	0.0004 (7)
C3	0.0280 (10)	0.0386 (10)	0.0242 (9)	−0.0105 (8)	0.0076 (8)	−0.0032 (8)
C4	0.0228 (10)	0.0597 (14)	0.0239 (10)	−0.0064 (9)	0.0046 (8)	0.0036 (9)
C5	0.0243 (9)	0.0515 (13)	0.0247 (10)	0.0086 (9)	0.0095 (8)	0.0073 (9)
C6	0.0285 (9)	0.0326 (10)	0.0222 (9)	0.0029 (8)	0.0122 (8)	0.0025 (8)
C7	0.0227 (9)	0.0270 (9)	0.0169 (8)	−0.0021 (7)	0.0082 (7)	0.0017 (7)
C8	0.0236 (9)	0.0226 (9)	0.0213 (9)	−0.0016 (7)	0.0065 (7)	−0.0024 (7)
C9	0.0176 (8)	0.0242 (9)	0.0234 (9)	−0.0024 (7)	0.0043 (7)	0.0033 (7)
C10	0.0206 (8)	0.0252 (9)	0.0223 (9)	0.0030 (7)	0.0076 (7)	0.0019 (7)
C11	0.0318 (10)	0.0286 (10)	0.0268 (10)	0.0002 (8)	0.0085 (8)	0.0069 (8)
C12	0.0286 (10)	0.0337 (10)	0.0214 (9)	−0.0015 (8)	0.0048 (8)	0.0047 (8)

Geometric parameters (Å, º)

Br1—C9	1.8687 (18)	C5—C6	1.400 (3)
Br2—C10	1.8766 (18)	C5—H5	0.9500
C1—C10	1.530 (2)	C6—C7	1.382 (3)
C1—C11	1.533 (3)	C6—H6	0.9500
C1—C2	1.533 (3)	C7—C8	1.530 (2)
C1—H1	1.0000	C8—C9	1.531 (2)
C2—C3	1.379 (3)	C8—C12	1.532 (3)
C2—C7	1.398 (3)	C8—H8	1.0000
C3—C4	1.399 (3)	C9—C10	1.318 (3)
C3—H3	0.9500	C11—C12	1.319 (3)
C4—C5	1.380 (3)	C11—H11	0.9500
C4—H4	0.9500	C12—H12	0.9500
C10—C1—C11	106.24 (15)	C6—C7—C2	120.79 (17)
C10—C1—C2	104.60 (14)	C6—C7—C8	126.99 (17)
C11—C1—C2	105.06 (15)	C2—C7—C8	112.22 (15)
C10—C1—H1	113.4	C7—C8—C9	104.32 (14)
C11—C1—H1	113.4	C7—C8—C12	105.75 (14)
C2—C1—H1	113.4	C9—C8—C12	106.20 (14)
C3—C2—C7	120.53 (18)	C7—C8—H8	113.3
C3—C2—C1	127.22 (17)	C9—C8—H8	113.3
C7—C2—C1	112.25 (15)	C12—C8—H8	113.3
C2—C3—C4	118.90 (19)	C10—C9—C8	113.85 (15)
C2—C3—H3	120.5	C10—C9—Br1	126.50 (14)
C4—C3—H3	120.5	C8—C9—Br1	119.41 (13)
C5—C4—C3	120.51 (18)	C9—C10—C1	113.88 (16)

C5—C4—H4	119.7	C9—C10—Br2	125.79 (14)
C3—C4—H4	119.7	C1—C10—Br2	120.20 (13)
C4—C5—C6	120.73 (19)	C12—C11—C1	114.00 (17)
C4—C5—H5	119.6	C12—C11—H11	123.0
C6—C5—H5	119.6	C1—C11—H11	123.0
C7—C6—C5	118.50 (19)	C11—C12—C8	113.66 (17)
C7—C6—H6	120.7	C11—C12—H12	123.2
C5—C6—H6	120.7	C8—C12—H12	123.2

C10—C1—C2—C3	123.85 (19)	C2—C7—C8—C12	−54.79 (19)
C11—C1—C2—C3	−124.47 (19)	C7—C8—C9—C10	−57.17 (19)
C10—C1—C2—C7	−55.32 (19)	C12—C8—C9—C10	54.3 (2)
C11—C1—C2—C7	56.35 (18)	C7—C8—C9—Br1	117.51 (14)
C7—C2—C3—C4	−0.1 (3)	C12—C8—C9—Br1	−131.03 (13)
C1—C2—C3—C4	−179.24 (17)	C8—C9—C10—C1	−0.4 (2)
C2—C3—C4—C5	1.5 (3)	Br1—C9—C10—C1	−174.62 (13)
C3—C4—C5—C6	−1.3 (3)	C8—C9—C10—Br2	175.36 (12)
C4—C5—C6—C7	−0.2 (3)	Br1—C9—C10—Br2	1.1 (2)
C5—C6—C7—C2	1.6 (3)	C11—C1—C10—C9	−53.6 (2)
C5—C6—C7—C8	−179.54 (17)	C2—C1—C10—C9	57.3 (2)
C3—C2—C7—C6	−1.4 (3)	C11—C1—C10—Br2	130.43 (14)
C1—C2—C7—C6	177.83 (16)	C2—C1—C10—Br2	−118.75 (14)
C3—C2—C7—C8	179.56 (16)	C10—C1—C11—C12	53.9 (2)
C1—C2—C7—C8	−1.2 (2)	C2—C1—C11—C12	−56.6 (2)
C6—C7—C8—C9	−121.96 (19)	C1—C11—C12—C8	0.0 (2)
C2—C7—C8—C9	57.00 (18)	C7—C8—C12—C11	56.5 (2)
C6—C7—C8—C12	126.26 (19)	C9—C8—C12—C11	−54.0 (2)