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# The 'cyclophene' [2.2.2](1,2,4)cyclophan-9-ene

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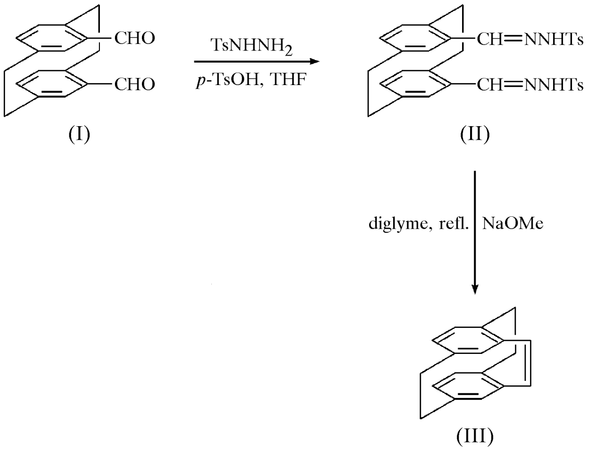
In the title compound, $C_{18}H_{16}$, the [2.2]paracyclophane geometry is restrained to a considerable extent despite the introduction of the extra C=C bridge; typical paracyclophane features, such as the elongated C—C bridges, are still observed. However, the bridgehead atoms of the C=C bridge are forced into unusually close proximity [2.657 (3) Å], which in turn causes the rings to be rotated to an interplanar angle of 13.7 (2)°. The packing involves hexagonally close-packed layers of molecules parallel to the $xy$ plane, corresponding to the known '7,11' pattern of paracyclophanes, but without significant short intermolecular contacts.

## Comment

In contrast to to the $[2_n]$cyclophanes with saturated bridges – from $[2_2]$paracyclophane (review article: Hopf & Kleinschroth, 1982) to superphane ($[2_6]$paracyclophane; review article: Gleiter & Roers, 2004) – relatively little is known about the chemical behavior and the structural properties of cyclophanes with unsaturated bridges ('cyclophenes'). We report here the preparation and the structural properties of [2.2.2](1,2,4)cyclophan-9-ene, (III), a triply bridged cyclophane in which one of the ethano bridges of its saturated analogue has been replaced by a double bond. The unsaturated analogue of superphane, superphene, a hydrocarbon with six adjacent unsaturated bridges, is so far unknown. A search of the Cambridge Structural Database (Allen, 2002) revealed no other cyclophene of the [2.2.2](1,2,4) type.



The molecule of (III) is shown in Fig. 1 and selected molecular dimensions are presented in Table 1. The molecule may be regarded as a derivative of [2.2]paracyclophane (bridgehead atoms C3, C6, C13 and C16); as we have previously noted in such derivatives with extra bridges (Bondarenko *et al.*, 2007), the molecular geometry is changed surprisingly little by the extra bridge. Typical features of [2.2]paracyclophanes are elongated single bonds in the bridges, widened $sp^3$ angles at the bridge atoms, narrowed $sp^2$ angles in the six-membered rings at the bridgehead atoms, and flattened boat conformations of the rings, with the bridgehead atoms displaced by *ca* 0.10–0.15 Å from the mean plane of the other four atoms towards the centre of the molecule. All these features are observed in (III) (Table 1), except that the deviations of the bridgehead atoms are slightly smaller [0.111 (3) Å for C3, 0.136 (3) Å for C6, 0.146 (4) Å for C13 and 0.115 (4) Å for C16].

However, whereas the rings in normal [2.2]paracyclophanes are parallel, those in (III) are significantly rotated, with an interplanar angle of 13.7 (2)°; this is also an effect that we have noted before (Bondarenko *et al.*, 2007) and is presumably connected with the extra C9=C10 bridge. The bridge is not elongated with respect to normal C=C distances, but the angles at the bridge atoms are significantly narrower than ideal $sp^2$ angles. This leads to an extremely short contact of 2.657 (3) Å between the formally nonbonded atoms C8 and C11, whereas the ring rotation causes atoms C4 and C5 to be farther than usual (> 3.2 Å) from their counterparts (Table 2).

The crystal packing involves layers of molecules parallel to the $xy$ plane, with four layers per cell at $z \simeq \frac{1}{8}, \frac{3}{8}, \frac{5}{8}$ and $\frac{7}{8}$. One such layer is shown in Fig. 2. The molecules are arranged in a hexagonally close-packed pattern; connecting the centroids of adjacent molecules, which are related by the $b$-glide planes, forms a rhombus with sides of *ca* 7.0 Å and angles of 66 and

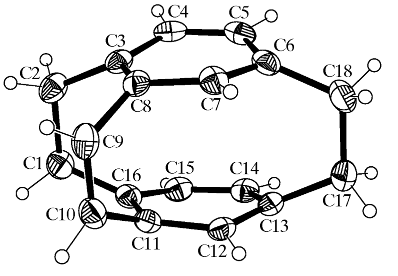


**Figure 1**
The molecule of (III). Displacement ellipsoids represent 30% probability levels.

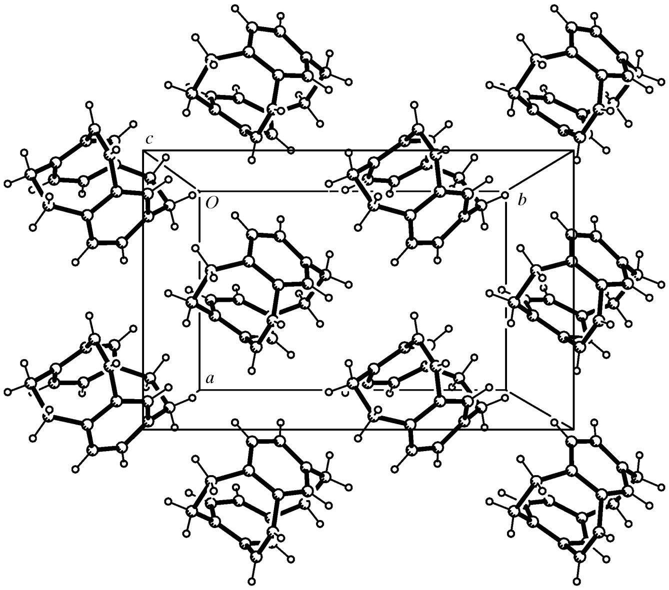


**Figure 2**
The packing of (III), viewed parallel to the $z$ axis in the region $z \simeq \frac{1}{8}$.

113°. The approximately equidimensional nature of the molecules of simple [2.2]paracyclophane derivatives often leads to such layer structures, in which the two cell constants associated with the layer are, as here, often *ca* 7 and 11 Å. We have called this the '7,11'-packing pattern (El Shaieb *et al.*, 2003; Jones *et al.*, 2007). In many cases, adjacent molecules are connected by C—H···$\pi$ contacts, sometimes extremely short, but in (III) there are no H···(C9=C10) contacts shorter than 3.17 Å and no H···ring centroid contacts greater than 3.34 Å.

## Experimental

For the preparation of the bis-tosylhydrazone (II) of the pseudo-geminal dialdehyde (I) (Bondarenko *et al.*, 2007, and references therein), a solution of (I) (1.5 g, 5.68 mmol) and *p*-toluenesulfonic acid hydrazide (3.0 g, 16.12 mmol) in anhydrous tetrahydrofuran (250 ml) was refluxed for 2 h in the presence of a trace of *p*-toluenesulfonic acid. After cooling to room temperature, the solvent was removed *in vacuo* and the raw product purified by plate chromatography on silica gel with dichloromethane/ethyl acetate (98:2 *v*/*v*). After recrystallization from dichloromethane/ethanol, (II) (3.13 g, 92%) was obtained as colourless needles [m.p. 467 K (decomposition)]. Analysis calculated for $C_{32}H_{32}N_4O_4S_2$ ($M_r$ = 600.76): C 63.98, H 5.36%; found: C 62.94, H 4.98%.

For the preparation of (III), a solution of (II) (3.0 g, 5.0 mmol) and sodium methoxide (3.0 g, 93 mmol) in diglyme (150 ml) was heated under reflux for 3 h. After cooling to room temperature, water (200 ml) was added and the reaction mixture was extracted with ether. The organic phase was separated and dried (calcium chloride), the solvent was removed by rotary evaporation, and the remainder was purified by plate chromatography on silica gel with tetrachloromethane/dichloromethane (9:1 *v*/*v*). After recrystallization from dichloromethane/ethanol, (III) (0.85 g, 73%) was obtained as colourless plates (m.p. 430–431 K). $^1$H NMR (400 MHz, $CD_2Cl_2$, int. TMS): $\delta$ 7.24 (*s*, 2H, 9-H), 6.39 (*dd*, $J_o$ = 7.9 Hz, $J_m$ = 2.1 Hz, 2H, 5-H), 6.33 (*d*, $J_o$ = 7.9 Hz, 2H, 4-H), 6.23 (*d*, $J_m$ = 2.1 Hz, 2H, 7-H), 3.05 (*m*, 4H, ethano bridge), 2.93 (*m*, 2H, ethano bridge), 2.61 (*m*, 2H, ethano bridge); $^{13}$C NMR (100.6 MHz, $CD_2Cl_2$): $\delta$ 141.98, 141.45, 139.60 (3 × *s*, quart. C), 139.21, 138.21, 133.47, 130.82 (4 × *s*, Ar—C, –HC=CH–), 35.42, 34.29 (*t*, ethano bridges). Analysis calculated for $C_{18}H_{16}$: C 93.06, H 6.94%; found: C 93.16, H 6.85%. Single crystals were obtained from cyclohexane. Additional spectroscopic data for (II) and (III) are given in the deposited material.

### *Crystal data*

$C_{18}H_{16}$
$M_r$ = 232.31
Orthorhombic, *Pbca*
$a$ = 7.6402 (15) Å
$b$ = 11.775 (2) Å
$c$ = 26.927 (5) Å
$V$ = 2422.4 (8) Å$^3$
$Z$ = 8
Mo $K\alpha$ radiation
$\mu$ = 0.07 mm$^{-1}$
$T$ = 153 (2) K
0.7 × 0.5 × 0.25 mm

### *Data collection*

Stoe Stadi-4 diffractometer
4154 measured reflections
2139 independent reflections
1446 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.059
3 standard reflections
frequency: 60 min
intensity decay: 5%

### *Refinement*

$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.150
$S$ = 1.10
2139 reflections
164 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max}$ = 0.23 e Å$^{-3}$
$\Delta\rho_{\rm min}$ = −0.24 e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| C1—C2 | 1.580 (4) | C17—C18 | 1.578 (4) |
| C9—C10 | 1.332 (4) | | |
| C16—C1—C2 | 112.4 (2) | C9—C10—C11 | 116.6 (2) |
| C3—C2—C1 | 112.6 (2) | C12—C13—C14 | 116.9 (2) |
| C8—C3—C4 | 118.1 (2) | C15—C16—C11 | 117.6 (2) |
| C7—C6—C5 | 117.2 (2) | C13—C17—C18 | 113.8 (2) |
| C10—C9—C8 | 115.9 (2) | C6—C18—C17 | 114.0 (2) |

**Table 2**
Contact distances between cyclophane rings (Å).

| | | | |
|---|---|---|---|
| C3···C16 | 2.737 (3) | C6···C13 | 2.807 (3) |
| C4···C15 | 3.326 (3) | C7···C12 | 2.831 (3) |
| C5···C14 | 3.280 (3) | C8···C11 | 2.657 (3) |

H-atom positions were calculated, after which the H atoms were refined using a riding model with C—H distances of 0.95 Å for $sp^2$ and 0.99 Å for $sp^3$ C atoms. $U_{\rm iso}$(H) values were fixed at 1.2$U_{\rm eq}$ of the parent C atoms. There is no significant residual electron density that might suggest disorder of the bridges. A rigid-body libration correction (Schomaker & Trueblood, 1968) gave an acceptable $R_{\rm lib}$ of 0.062 and bond-length corrections of 0.005–0.006 Å; corrected bond lengths are given in the deposited CIF, but uncorrected values are used in Table 1 and the *Comment* section.

Data collection: *DIF4* (Stoe & Cie, 1992); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3070). Services for accessing these data are described at the back of the journal.

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