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

N2—C3	1.306 (2)	C4—N3	1.349 (2)
N2—N4	1.362 (2)	N3—C3	1.321 (3)
C4—N4	1.294 (2)		
C3—N2—N4	110.99 (15)	N2—C3—N3	107.22 (17)
N4—C4—N3	111.53 (17)	C4—N4—N2	103.76 (14)
C3—N3—C4	106.50 (15)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H01···N1	0.74 (3)	2.04 (3)	2.7576 (19)	166 (3)
N3—H02···O3^{i}	0.91 (3)	2.47 (2)	2.997 (2)	117 (2)
N3—H02···O4^{ii}	0.91 (3)	2.04 (3)	2.8415 (19)	146 (2)
C3—H3···O1^{iii}	0.81 (2)	2.26 (2)	3.046 (2)	161 (2)
C4—H4···O3^{i}	0.95 (2)	2.42 (2)	2.974 (2)	117 (2)
C4—H4···O2^{iv}	0.95 (2)	2.58 (2)	3.076 (2)	113 (2)
C1—H1*C*···N4^{v}	0.98	2.81	3.777 (2)	168
C2—H2*C*···N4^{vi}	0.98	2.80	3.503 (2)	130

Symmetry codes: (i) $-x, 1-y, \frac{1}{2}+z$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}+z$; (iii) $x-\frac{1}{2}, \frac{1}{2}-y, z$; (iv) $1-x, 1-y, \frac{1}{2}+z$; (v) $\frac{1}{2}+x, \frac{3}{2}-y, z$; (vi) $1-x, 1-y, z-\frac{1}{2}$.

Methyl groups were identified from difference syntheses and refined as rigid groups allowed to rotate but not tip. Other H atoms were refined freely. The origin was fixed by the method of Flack & Schwarzenbach (1988). The absolute structure was determined from 1072 Friedel pairs.

Data collection: *DIF*4 (Stoe & Cie, 1992*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*97.

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Heterocycle-substituted [2.2]paracyclophanes

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Abstract

The observed geometries of the cyclophane groups of 4-(2′-furyl)[2.2]paracyclophane [systematic name: 5-(2-furyl)tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene], $C_{20}H_{18}O$, and 5-(2′-thienyl)[2.2]paracyclophane [systematic name: 5-(2-thienyl)tricyclo[8.2.2.2^{4,7}]hexadeca-4,6,10,12,13,15-hexaene], $C_{20}H_{18}S$, are very similar both to the skeleton of the parent compound and to [2.2]paracyclophane fragments in other structures; the bridgehead C atoms are characteristically bent out of the plane of the other four coplanar atoms building the typical boat conformation of the aromatic rings in [2.2]-paracyclophanes. These rings are twisted with respect to each other. The thiophene ring of (2) is disordered over two positions, which could however be well resolved. The heterocyclic substituents are rotated out of the plane of the four coplanar C atoms C4, C5, C7 and C8 by 25.1 (1)° in (1), and 34.7 (6) and 32.9 (6)° in (2) for both positions of disorder.

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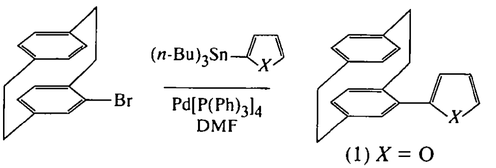
Comment

To the best of our knowledge, the two title compounds are the first examples of heterocyclic 4-substituted [2.2]-paracyclophanes to be structurally characterized. We are interested in the electronic conditions of the π-system in the [2.2]paracyclophane and the heterocyclic groups. In order to investigate the extent of the π-system, we have carried out corresponding X-ray structure determinations of 4-(2′-furyl)[2.2]paracyclophane, (1), and 4-(2′-thienyl)[2.2]paracyclophane, (2). The deformations of the aromatic rings in the [2.2]paracyclophane groups are similar in both compounds; they are distorted in the same way as in the parent compound, (3) (Keehn, 1983; Stalke, 1999). The C atoms bearing the methylene bridges are bent out of the plane of the other four atoms into a boat conformation. These planes are nearly parallel to each other, with interplanar angles within the [2.2]-paracyclophane groups of 0.09 (2)° in (1) and 0.68 (14)° in (2); the parent compound (3) shows exactly parallel planes (crystallographic inversion symmetry). The inter-benzenoid distances between the planes specified by the two sets of four coplanar C atoms range from 3.061 (4) to 3.087 (3) Å in (1), and from 3.060 (3) to 3.093 (3) Å in (2). The bridgehead C atoms C3· · ·C14 and C6· · ·C11 are separated by 2.774 (4) and 2.764 (4) Å in (1), and by 2.779 (3) and 2.762 (3) Å in (2). The corresponding values in the parent compound (3) amount to 2.779 Å for the bridgehead distance and 3.093 Å for the inter-ring contact (Stalke, 1999).



(1) X = O
(2) X = S

The twist of the aromatic rings with respect to one another, represented by the torsion angle C9· · ·C2—C1· · ·C10, amounts to −4.9 (1)° in (1) and 2.1 (1)° in (2).

As expected, the furan and thiophene rings are nearly planar, with mean deviations from planarity of 0.002 Å in (1), and 0.004 (C2′—S) and 0.007 Å (C2′—S″) in (2). The thiophene ring is disordered over two positions with occupancies of 51.4 (3) and 48.6 (3). These positions are related by a rotation of 177.6 (12)° about the C4—C2′ bond. The model employed for the disorder shows an acceptable geometry for both thiophene rings, but the bond lengths deviate from the data obtained for thiophene by electron diffraction (Harshbarger & Bauer, 1970).

Perhaps surprisingly, the furan ring is not disordered. This may be associated with intermolecular interactions between the oxygen of the furan and a C—H group of another molecule. The shortest such contact is C7—H7· · ·O($\frac{1}{2}+x$, $\frac{3}{2}-y$, $\frac{1}{2}+z$), with O· · ·H = 2.73, O· · ·C = 3.384 (4) Å and C—H· · ·O =126°. The angle is rather narrow, but Desiraju (1996) suggests that C—H· · ·O contacts below 2.8 Å can be accepted as hydrogen bonds.

Within the estimated standard deviations of the bond lengths and angles, the geometry of the furan ring in (1) is in good agreement with the data reported by Allen *et al.* (1987) and with values found in other compounds containing a furan fragment (SEZPUI: Lokaj *et al.*, 1990; KINJIA: Lokaj *et al.*, 1991; RUPTAX: Hashmi *et al.*, 1997; NOZTOL: Lokaj *et al.*, 1998).

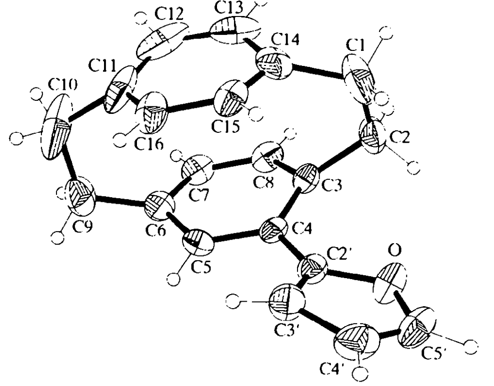


Fig. 1. The molecule of compound (1) in the crystal. Ellipsoids correspond to 50% probability levels. H-atom radii are arbitrary.

The C4—C2′ single bond in both compounds is in the range of the standard value of a non-conjugated Csp^2—Csp^2 single bond [1.476 Å; Allen *et al.*, 1987], with a value of 1.467 (4) in (1) and 1.475 (2) Å in (2). The heterocyclic substituents are rotated out of the mean plane of the four coplanar C atoms (C4—C5—C7—C8, r.m.s. deviations 0.004 Å) by 25.1 (1) Å in (1), and by 34.7 (6) and 32.9 (6) Å in (2) for the two positions of disorder. Obviously the π-systems in both compounds are not delocalized between the [2.2]paracyclophane groups and the heterocyclic substituents.

Larger interplanar angles are observed in carbonyl-bridged compounds with aromatic substituents: 63.5 (1)° in 4-benzoyl[2.2]paracyclophane and 62.9 (1)° in 4-(2′-naphthoyl)[2.2]paracyclophane (Jones *et al.*, 1995).

The orientation of the paracyclophane groups and the heterocycles can be described by the torsion angle C5—C4—C2′—C3′. Both compounds are twisted out of the *syn-* (or *anti-*) periplanar conformation by about 30° [C5—C4—C2′—C3′ −21.9 (4)° in (1), and C5—C4—C2′—C3′ −31.9 (10)° and C5—C4—C2″—C3″ 143.7 (9)° in (2)]. This deviation from the best form for delocalization is smaller than in 4-benzoyl[2.2]-

paracyclophane [C5—C4—C17—C18 45.0 (2)°] and 4-(2′-naphthoyl)[2.2]paracyclophane [C5—C4—C17—C18 40.8 (5)°] (Jones *et al.*, 1995).

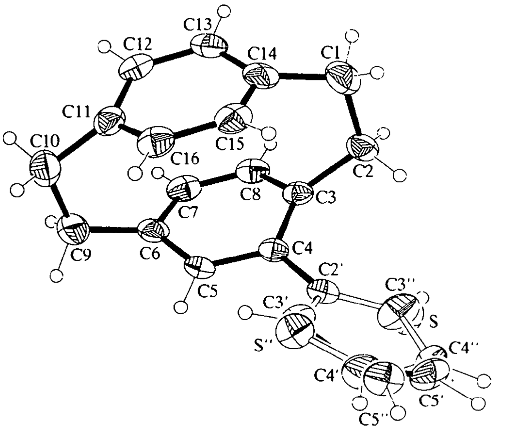


Fig. 2. The molecule of compound (2) in the crystal with both components of disorder. Ellipsoids correspond to 50% probability levels. H-atom radii are arbitrary.

Experimental

4-Bromo[2.2]paracyclophane (1.44 g, 5.01 mmol), 2-(tri-*n*-butylstannyl)furan (1.58 ml, 5.02 mmol) and tetrakis(triphenylphosphine)palladium(0) (90 mg, 0.078 mmol), as catalyst, were stirred in dry *N*,*N*-dimethylformamide (DMF) (15 ml) at 393 K for 6 d (Palmisano & Santagostino, 1993). After removal of solvent *in vacuo*, the residue was taken up in dichloromethane (50 ml) and stirred overnight with 10% aqueous KF solution (30 ml) (Leibner & Jacobus, 1979). After filtration, the organic layer was washed with water, dried over $MgSO_4$ and evaporated. Column chromatography (SiO_2; pentane/dichloromethane 6:1) and crystallization at room temperature from dichloromethane/methanol gave (1) in 66% yield as a colourless solid (910 mg, m.p. 376–368 K). An equivalent procedure gave (2) in 58% yield (844 mg, m.p. 409–410 K). A solution of 4-bromo[2.2]paracyclophane (1.44 g, 5.01 mmol), 2-(tri-*n*-butylstannyl)thiophene (1.59 ml, 5.01 mmol) and tetrakis(triphenylphosphine)palladium(0) (90 mg, 0.078 mmol) were stirred in dry DMF (15 ml) at 393 K for 5 h followed by a work-up as above. Slow evaporation of a dichloromethane/methanol solution yielded colourless crystals.

Compound (1)

Crystal data

$C_{20}H_{18}O$
$M_r = 274.34$
Monoclinic
Cc
$a = 7.4177 (8)$ Å
$b = 21.393 (2)$ Å
$c = 9.2734 (10)$ Å
$\beta = 101.766 (8)°$
$V = 1440.7 (3)$ Å^3
$Z = 4$
$D_x = 1.265$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 49 reflections
$\theta = 5.8–12.5°$
$\mu = 0.076$ mm^{-1}
$T = 173 (2)$ K
Prism
$0.60 \times 0.42 \times 0.24$ mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
3502 measured reflections
1655 independent reflections
1459 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.020$

$\theta_{\rm max} = 27.49°$
$h = -9 \rightarrow 0$
$k = -27 \rightarrow 27$
$l = -11 \rightarrow 12$
3 standard reflections every 247 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.125$
$S = 1.062$
1655 reflections
190 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0761P)^2 + 0.4053P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.29$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.30$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C4—C2′	1.467 (4)		
C5—C4—C2′—C3′	−21.9 (4)	C9—C2—C1—C10	−4.91 (11)

Compound (2)

Crystal data

$C_{20}H_{18}S$
$M_r = 290.40$
Monoclinic
$P2_1/c$
$a = 16.850 (2)$ Å
$b = 7.6203 (10)$ Å
$c = 11.574 (2)$ Å
$\beta = 95.523 (11)°$
$V = 1479.3 (4)$ Å^3
$Z = 4$
$D_x = 1.304$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 63 reflections
$\theta = 5.2–11.4°$
$\mu = 0.209$ mm^{-1}
$T = 173 (2)$ K
Tablet
$0.86 \times 0.38 \times 0.15$ mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
2773 measured reflections
2590 independent reflections
1641 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.015$

$\theta_{\rm max} = 24.99°$
$h = -20 \rightarrow 1$
$k = -9 \rightarrow 0$
$l = -13 \rightarrow 13$
3 standard reflections every 247 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.084$
$S = 0.862$
2590 reflections
227 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0418P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.15$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (2)*

C4—C2′	1.475 (2)		
C5—C4—C2′—C3′	−31.9 (10)	C9—C2—C1—C10	2.10 (5)
C5—C4—C2′—C3″	143.7 (9)		

All H atoms were refined using a riding model. In order to obtain a better data/parameter ratio for (1), 203 similarity restraints were applied to the *U* components of C atoms. For (2), a system of 301 restraints was employed. The thiophene ring in (2) is disordered in the crystal and was refined on two positions of occupancies 0.514 (3) and 0.486 (3). The final model file with details of disorder restraints is included in the deposited material.

In (1), the origin was fixed according to the method of Flack & Schwarzenbach (1988). The absolute structure cannot be determined because the anomalous scattering is too small [the Flack (1983) parameter is indeterminate]. Friedel opposites were therefore merged before refinement.

For both compounds, data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1314). Services for accessing these data are described at the back of the journal.

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A racemic strigol analogue at 100 K

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Abstract

DL-3-[(2,5-Dihydro-3-methyl-2-oxo-5-furyl)oxymethylene]-3,3a,6,6a-tetrahydro-2*H*-cyclopenta[*b*]furan-2-one, $C_{13}H_{12}O_5$, has relative configurations at the asymmetric C atoms of 3a*S*, 6a*S* and 5′*R*. The dihedral angle formed by the fused cyclopentene and furan rings is 114.81 (5)°, and these rings form dihedral angles of 119.53 (5) and 67.68 (5)°, respectively, with the methylfuranone ring.

Comment

Witchweed (*Striga* species) is an angiospermous obligate root parasite that attacks corn, sorghum, sugarcane, rice and more than 60 other important crop plants and weeds of the grass family (Worsham, 1987). These beautifully adapted parasitic weeds occur commonly in the eastern hemisphere and inflict serious crop damage in many parts of the world (Johnson *et al.*, 1976). Their life-cycle is closely coupled to their environment and to their host. It is difficult to control *Striga* species because they produce tiny seeds in vast amounts that can remain viable in the soil for as long as 20 years. The seeds will germinate only when stimulated by a chemical exuded from the roots of the host crops (Rugutt, 1996). When the *Striga* stimulant, strigol (Cook *et al.*, 1972), was isolated from cotton (*Gossypium hirsutum* L.), a non-host plant, the possibility of weed control by introduction into the soil of a synthetic stimulant to induce suicidal germination of seeds of the parasite was revived. Therefore, considerable effort has been put into the preparation of simpler but structurally related strigol analogues that retain high germination activity (MacAlphine *et al.*, 1976; Johnson *et al.*, 1976). One such strigol analogue,