

C—H··· π interactions in five ethynyl-substituted [2.2]paracyclophanes: further examples of the '7,11' packing pattern

Peter G. Jones,^{a*} Ina Dix^{b‡} and Henning Hopf^b

^aInstitut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany, and ^bInstitut für Organische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany
Correspondence e-mail: p.jones@tu-bs.de

Received 31 May 2007

Accepted 5 June 2007

Online 14 July 2007

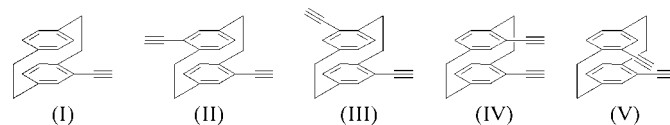
The monosubstituted derivative 4-ethynyl[2.2]paracyclophane, C₁₈H₁₆, (I), and the four disubstituted isomers, 4,12-, (II), 4,13-, (III), 4,15-, (IV), and 4,16-diethynyl[2.2]paracyclophane, (V), all C₂₀H₁₆, show the usual distortions of the [2.2]paracyclophane framework. The crystal packing is analyzed in terms of C—H··· π interactions, some with H··· π as short as 2.47 Å, in which the cyclophane rings and/or the triple-bond systems may act as acceptors. For compounds (I) and (IV), the known '7,11'-type cyclophane packing is observed, with a herring-bone pattern of molecules in a layer structure.

Comment

We recently described the syntheses of 4-ethynyl[2.2]paracyclophane, (I), and the four isomeric disubstituted derivatives, 4,12-diethynyl-, (II), 4,13-diethynyl-, (III), 4,15-diethynyl-, (IV), and 4,16-diethynyl[2.2]paracyclophane, (V) (Bondarenko *et al.*, 2004). These molecules are interesting building blocks for molecular scaffolding (Hopf & Dix, 2006). We are also interested in the structures of paracyclophane derivatives and, in particular, in their packing, and have presented a description of C—H··· π interactions (Desiraju & Steiner, 1999) in some pseudo-geminally substituted derivatives (El Shaieb *et al.*, 2003). We present here the crystal structures of compounds (I)–(V). The disubstituted compounds (II), (III), (IV) and (V) represent the substitution patterns pseudo-*para*, pseudo-*meta*, pseudo-geminal and pseudo-*ortho*, respectively. To the best of our knowledge, this is the first time that all four possible isomers with a given substituent have been structurally characterized by X-ray methods.

[‡] Current address: Institut für Anorganische Chemie, Universität Göttingen, Tammannstrasse 4, 37077 Göttingen, Germany.

The molecules of compounds (I)–(V) are shown in Figs. 1–5. Those of (I), (III) and (V) are chiral, although all bulk samples were racemates. Nevertheless, compounds (III), (IV) and (V)



crystallize by chance in chiral space groups. Compound (II) crystallizes with two independent molecules, each of which displays imposed inversion symmetry; for this reason, the standard IUPAC numbering cannot be fully implemented for (II). For compound (V), the enantiomer in Fig. 5 is opposite to that in the scheme.

Bond lengths and angles may be considered normal. In particular, the molecules show the 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

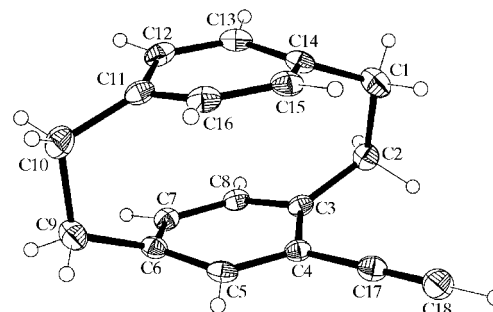


Figure 1
The molecular structure of compound (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

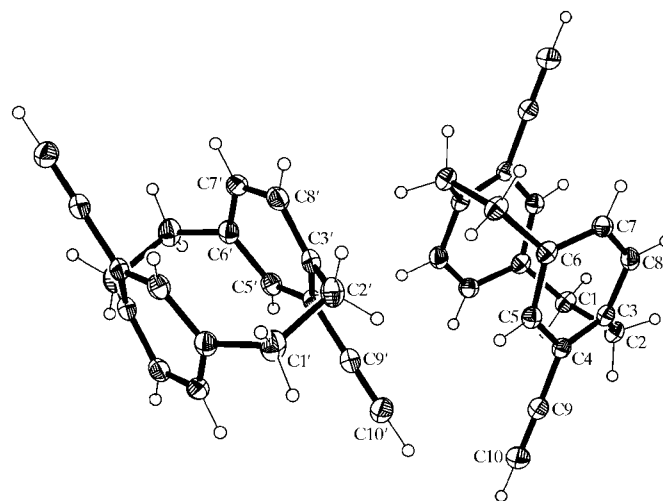


Figure 2
The two independent molecules of compound (II) (each with inversion symmetry), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The label for atom C4' has been omitted for clarity.

(the bridgehead atoms lie significantly out of the plane of the other four ring atoms). These dimensions are summarized in Table 1. In the pseudo-geminal isomer, (IV), the separations between the atoms of the eclipsed triple-bond systems are $C4 \cdots C15 = 3.170(2) \text{ \AA}$, $C17 \cdots C19 = 3.371(2) \text{ \AA}$ and $C18 \cdots C20 = 3.642(3) \text{ \AA}$. We have utilized such close contacts in related derivatives with double bonds to form ladderanes (see, for example, Hopf *et al.*, 2005).

The molecular packing of all five compounds can be analysed in terms of $C-H \cdots \pi$ interactions, where the acceptor system can be the triple bond or the π electron density of the rings (Desiraju & Steiner, 1999). A summary of the observed contacts is given in Table 2. The packing of compound (I) involves layers of molecules parallel to the *ab* plane at $z \simeq \frac{1}{4}, \frac{3}{4}$, etc. One such layer is shown in Fig. 6. The molecules adopt a herring-bone-type pattern, within which the three $C-H \cdots \pi$ interactions are accommodated. We have previously pointed out (El Shaieb *et al.*, 2003) that many simple derivatives of [2.2]paracyclophane display a common combination of two axis lengths, one of *ca* 7.5 Å and the other of *ca* 11.5 Å. These values are consistent with the formation of hydrogen-bonded layers such as that observed for (I). Because the molecules are approximately equidimensional, mutual rotations within the layer can be tolerated without disturbing

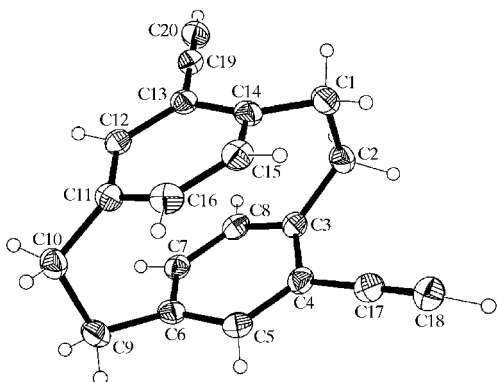


Figure 3
The molecular structure of compound (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

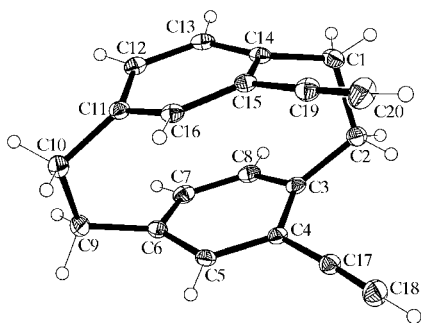


Figure 4
The molecular structure of compound (IV), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

the overall pattern, and thus different types of H atom (bridge or ring) can act as donors. The substituents play a less important role: in general, they are directed perpendicularly away from the layers, and thus determine the interlayer interactions and, in turn, the space group and third axis length. The only requirement is that the substituents should not be too large or themselves determine the most important secondary interactions. In compound (I), the ethynyl substituent is even capable of accepting a hydrogen bond within the layer without disturbing the 7,11 pattern.

For the ring systems, it is not always clear whether the whole ring or only a part of it is the 'true' acceptor of the hydrogen bond. For compound (I), the acceptor system of hydrogen bond 2 might be better expressed as the triangle of atoms C11/C12/C16 forming one angled end of the 'boat'. For this grouping, the hydrogen-bond parameters would be 2.69 Å and 168°, shorter and more linear than the formal contact to the ring centroid.

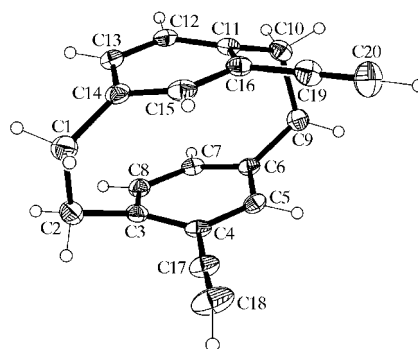


Figure 5
The molecular structure of compound (V), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

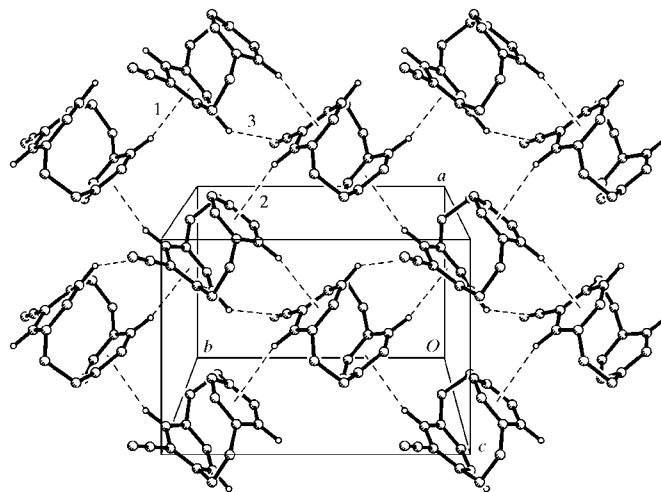


Figure 6
A packing diagram for compound (I), viewed perpendicular to the *ab* plane. Hydrogen bonds are shown as dashed lines and are numbered according to Table 2. The packing is of the 7,11 type (see *Comment*).

The packing of compound (II) is shown in Fig. 7. It too involves a layer structure, but the 7,11 pattern is not observed. Instead, hydrogen bonds 1 and 2 (the latter involving an ethynyl acceptor) combine in layers parallel to (101). The other two hydrogen bonds are formed between layers. The acceptor for hydrogen bond 3 might be better expressed as the centroid of atoms C5–C7 (2.66 Å and 134°). Hydrogen bond 4 is a borderline case.

The 3_1 axis of compound (III) is clearly recognisable in the packing diagram shown in Fig. 8. Within the 3_1 helices, the

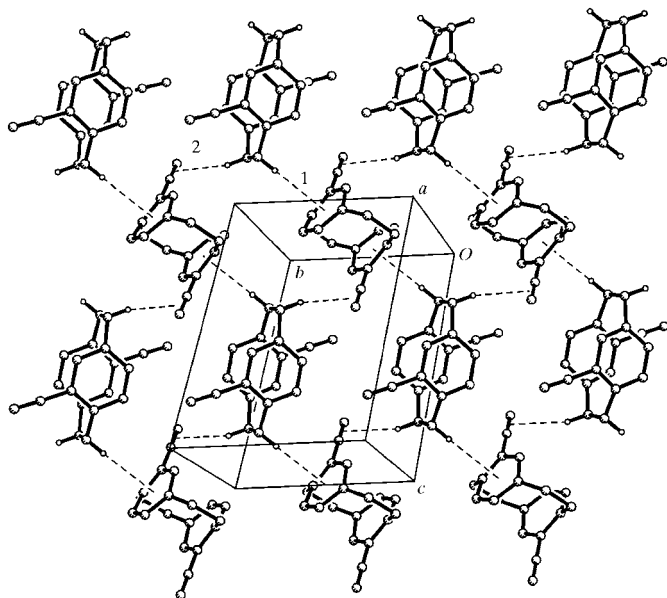


Figure 7
A packing diagram for compound (II), viewed perpendicular to (101) in the region $x, z \simeq \frac{1}{4}$. Hydrogen bonds are shown as dashed lines and are numbered according to Table 2. The top horizontal row of molecules involves only the first independent molecule, the next row only the second independent molecule, etc.

short hydrogen bond 1, with an ethynyl H atom as donor, links successive molecules (the 'true' acceptor might be the centroid of atoms C11/C12/C16, with hydrogen-bond parameters of 2.56 Å and 138°). The other three hydrogen bonds, one short and two long, link adjacent helices. It is noteworthy that hydrogen bond 3 is from an ethynyl group to a symmetry equivalent of the same group.

With compound (IV), a return to the 7,11 pattern is observed (Fig. 9), with one very short hydrogen bond (No. 1). The ethynyl groups play no role within the layer, but instead are involved in interlayer contacts.

Compound (V) crystallizes, like (III), in the space group $P3_1$. The packing diagram (Fig. 10) shows that the helices are assembled *via* a different type of hydrogen bond from those in

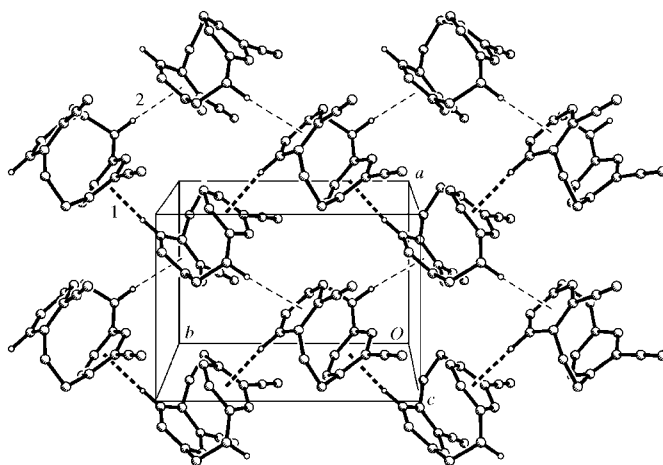


Figure 9
A packing diagram for compound (IV), viewed perpendicular to the ab plane. Hydrogen bonds are shown as dashed lines (thick for the short hydrogen bond 1 and thin for the long hydrogen bond 2). The packing is of the 7,11 type (see *Comment*).

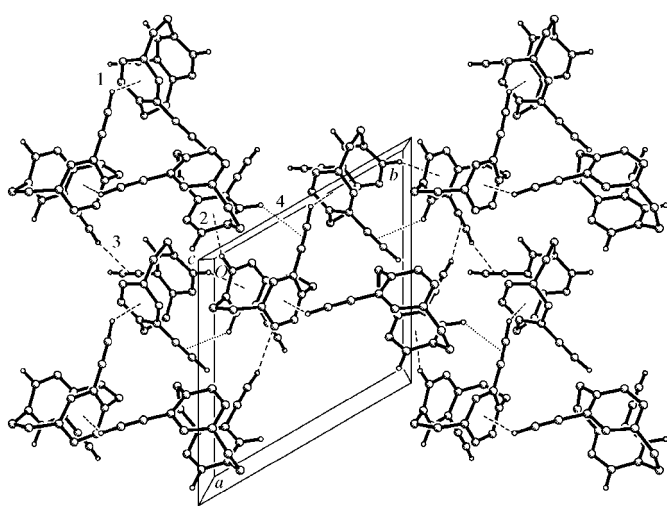


Figure 8
A packing diagram for compound (III), viewed parallel to the c axis. Hydrogen bonds are shown as dashed lines (dotted for the long bent hydrogen bond 4).

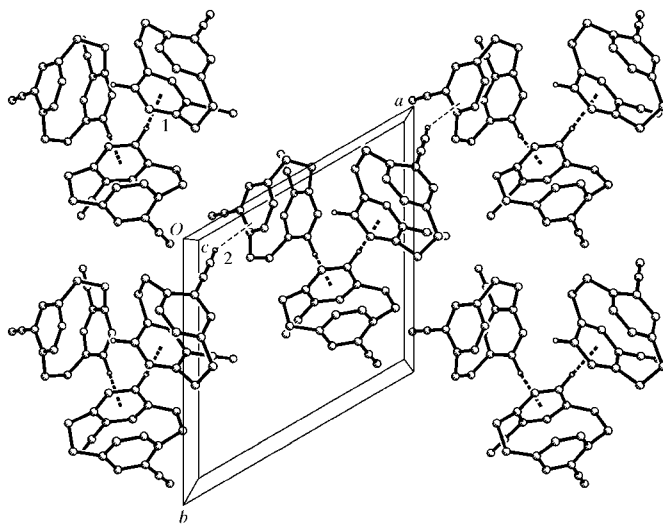


Figure 10
A packing diagram for compound (V), viewed parallel to the c axis. Hydrogen bonds are shown as dashed lines (thick for the short hydrogen bond 1 and thin for the long hydrogen bond 2).

(III), with a ring H atom as donor to the symmetry equivalent of the same ring. The first impression is that this is the only significant interaction (no other centroids or triple bonds appear to be involved in short contacts), but closer inspection reveals that the atom grouping C11/C12/C16 is the acceptor for hydrogen bond 2, which links adjacent helices.

Experimental

The preparations of compounds (I)–(V) from the aldehyde precursors by Wittig, Corey–Fuchs and Bestmann reactions, including characterization by spectroscopic and analytical methods, were described previously by us (Bondarenko *et al.*, 2004).

Compound (I)

Crystal data

C₁₈H₁₆
M_r = 232.31
 Monoclinic, *P*2₁/*c*
a = 7.6538 (14) Å
b = 11.022 (2) Å
c = 15.056 (3) Å
 β = 99.561 (16)°
V = 1252.4 (4) Å³
Z = 4
 Mo *K*α radiation
 μ = 0.07 mm⁻¹
T = 173 (2) K
 0.6 × 0.3 × 0.18 mm

Data collection

Siemens P4 diffractometer
 3461 measured reflections
 2191 independent reflections
 1267 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.024
 3 standard reflections
 every 247 reflections
 intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.103$
S = 0.86
 2191 reflections
 168 parameters
 167 restraints
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.19 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.17 \text{ e } \text{Å}^{-3}$

Compound (II)

Crystal data

C₂₀H₁₆
M_r = 256.33
 Triclinic, *P*1̄
a = 7.6316 (10) Å
b = 7.8177 (10) Å
c = 12.4446 (16) Å
 α = 78.125 (2)°
 β = 72.339 (2)°
 γ = 73.971 (2)°
V = 673.90 (15) Å³
Z = 2
 Mo *K*α radiation
 μ = 0.07 mm⁻¹
T = 143 (2) K
 0.42 × 0.28 × 0.26 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 5064 measured reflections
 3383 independent reflections
 2953 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.126$
S = 1.08
 3383 reflections
 189 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.35 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.23 \text{ e } \text{Å}^{-3}$

Compound (III)

Crystal data

C₂₀H₁₆
M_r = 256.33
 Trigonal, *P*3₁
a = 11.8823 (12) Å
c = 8.4426 (12) Å
V = 1032.3 (2) Å³
Z = 3
 Mo *K*α radiation
 μ = 0.07 mm⁻¹
T = 143 (2) K
 0.40 × 0.20 × 0.08 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 13844 measured reflections
 1719 independent reflections
 1536 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.081

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.088$
S = 1.02
 1719 reflections
 189 parameters
 185 restraints
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.22 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.14 \text{ e } \text{Å}^{-3}$

Compound (IV)

Crystal data

C₂₀H₁₆
M_r = 256.33
 Monoclinic, *P*2₁
a = 7.6187 (10) Å
b = 10.8231 (16) Å
c = 8.6293 (12) Å
 β = 101.230 (6)°
V = 697.93 (17) Å³
Z = 2
 Mo *K*α radiation
 μ = 0.07 mm⁻¹
T = 143 (2) K
 0.40 × 0.20 × 0.18 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 7442 measured reflections
 1821 independent reflections
 1706 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.049

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.098$
S = 1.07
 1821 reflections
 189 parameters
 185 restraints
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.26 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.16 \text{ e } \text{Å}^{-3}$

Compound (V)

Crystal data

C₂₀H₁₆
M_r = 256.33
 Trigonal, *P*3₁
a = 12.5475 (12) Å
c = 7.8705 (10) Å
V = 1073.1 (2) Å³
Z = 3
 Mo *K*α radiation
 μ = 0.07 mm⁻¹
T = 143 (2) K
 0.45 × 0.12 × 0.11 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
 14432 measured reflections
 1462 independent reflections
 1311 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.101$
S = 1.05
 1462 reflections
 189 parameters
 185 restraints
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.27 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.12 \text{ e } \text{Å}^{-3}$

Table 1
Selected dimensions of compounds (I)–(V) (Å, °).

Angles are rounded where necessary to nearest 0.1°. Unless otherwise specified, atom labels for columns 2–7, respectively, are: C1–C2 and C9–C10; angles at C1, C2, C9 and C10; angles at C3, C6, C11 and C14; deviations of atoms C3, C6, C11 and C14 from ring planes calculated without bridgehead atoms; bond lengths C17≡C18 and C19≡C20; angles C4–C17≡C18 and C–C19≡C20.

Compound	C–C bridge bond lengths	C–C–C bridge bond angles	C–C–C bridgehead bond angles	Bridgehead deviations from the plane	C≡C bond lengths	C–C≡C bond angles
(I)	1.582 (3)	111.8 (2)	117.8 (2)	0.162 (2)	1.183 (3)†	179.6 (2)†
	1.576 (3)	113.0 (2)	116.9 (2)	0.148 (2)		
		112.5 (2)	116.7 (2)	0.150 (3)		
(II)‡	1.599 (2)	113.0 (1)	117.2 (1)	0.149 (2)	1.194 (2)	178.1 (1)
	1.591 (2)	112.4 (1)	117.5 (1)	0.152 (2)	1.194 (2)	179.3 (1)
		112.9 (1)	116.9 (1)	0.157 (2)		
(III)	1.591 (3)	111.8 (2)	117.2 (2)	0.158 (3)	1.197 (3)	179.3 (2)
	1.587 (3)	112.1 (2)	117.2 (2)	0.148 (3)	1.188 (3)	177.0 (2)
		112.6 (2)	116.9 (2)	0.147 (3)		
(IV)	1.586 (2)	112.2 (1)	117.0 (1)	0.165 (2)	1.191 (3)	176.6 (2)
	1.584 (3)	112.6 (1)	117.1 (1)	0.155 (2)	1.191 (3)	177.5 (2)
		112.2 (1)	117.2 (1)	0.156 (2)		
(V)	1.585 (4)	112.4 (2)	116.8 (2)	0.150 (3)	1.187 (4)	177.6 (3)
	1.590 (3)	112.2 (2)	117.1 (2)	0.153 (3)	1.183 (4)	178.8 (3)
		112.4 (2)	117.2 (2)	0.150 (3)		
		112.5 (2)	117.3 (2)	0.154 (3)		

† For compound (I), there is only one triple bond. ‡ For compound (II), values are given for the first and second independent half-molecule (in that order), whereby atom labels can be taken from Fig. 2.

Table 2
C–H···π interactions (Å, °).

C–H distances are normalized to 1.08 Å (Steiner, 1998). Hydrogen-bond numbers are shown in the packing diagrams. Cg1 is the centroid of atoms C4/C5/C7/C8, Cg2 is the centroid of atoms C12/C13/C15/C16, Cg3 is the mid-point of C17≡C18 and Cg4 is the mid-point of C19≡C20.

Compound	No.	D–H···A	H···A	D–H···A	Symmetry code
(I)	1	C13–H13···Cg1	2.67	165	(1 – x, –½ + y, ½ – z)
	2	C5–H5···Cg2	2.86	131	(–x, ½ + y, ½ – z)
	3	C8–H8···Cg3	2.82	130	(1 – x, –½ + y, ½ – z)
(II)	1	C2–H2B···Cg2†	2.78	173	(–x, –y, 1 – z)
	2	C1–H1B···Cg4‡	2.80	164	(–x, 1 – y, 1 – z)
	3	C10'–H10'···Cg1	2.68	116	(1 – x, –y, 1 – z)
(III)	1	C2'–H2'2'···Cg3†	3.06	147	(1 – x, –y, 1 – z)
	2	C7–H7···Cg1	2.60	119	(y–x, 1 – x, –½ + z)
	3	C18–H18···Cg3	2.56	158	(–y, x – y, ½ + z)
(IV)	1	C18–H18···Cg3	2.91	173	(1 + y – x, 1 – x, –½ + z)
	2	C5–H5···Cg4	2.97	131	(y–x, –x, –½ + z)
	3	C8–H8···Cg2	2.47	155	(–x, ½ + y, 1 – z)
(V)	1	C10–H10B···Cg1	2.86	170	(1 – x, –½ + y, 1 – z)
	2	C20–H20···Cg3	2.75	139	(1 – x, –½ + y, 2 – z)
	3	C12–H12···Cg4	2.91	127	(–x, ½ + y, 1 – z)
(V)	1	C7–H7···Cg1	2.43	157	(1 – x + y, 1 – x, –½ + z)
	2	C20–H20···Cg2‡	2.78	149	(1 – x + y, 2 – x, ½ + z)

† Exceptions for compound (II): Cg2 is the centroid of atoms C4'/C5'/C7'/C8', Cg3 is the mid-point of C9–C10 and Cg4 is the mid-point of C9'–C10'. ‡ Exception for compound (V): Cg2 is the centroid of atoms C11/C12/C16 (see *Comment*).

Acetylenic H atoms were refined freely. Other H atoms were included using a riding model, with C–H bond lengths fixed at 0.99 (methylene) or 0.95 Å (*Csp*²) and with *U*_{iso}(H) = 1.2*U*_{eq}(C). For compounds (III)–(V), which crystallize in noncentrosymmetric space groups, the anomalous scattering was negligible, and Friedel opposite reflections were therefore merged. For this reason, the Flack (1983)

parameters are indeterminate. For compounds (III) and (V), this additionally means that the space groups *P*3₁ and *P*3₂ could not be distinguished. For consistency, *P*3₁ was chosen for both, which means that the enantiomer of (V) is opposite to that shown in the scheme (as noted in the *Comment*). For compounds (III)–(V), and additionally for compound (I), which diffracted weakly, restraints to displacement

parameters were employed (SIMU and DELU instructions in *SHELXL97*; Sheldrick, 1997) because the ratio of 'observed' reflections to parameters was poor (<10).

Data collection: *XSCANS* (Siemens, 1991) for (I); *SMART* (Bruker, 1998) for (II)–(V). Cell refinement: *XSCANS* for (I); *SAINT* (Bruker, 1998) for (II)–(V). Data reduction: *XSCANS* for (I); *SAINT* for (II)–(V). For all compounds, 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: GD3118). Services for accessing these data are described at the back of the journal.

References

- Bondarenko, L., Dix, I., Hinrichs, H. & Hopf, H. (2004). *Synthesis*, pp. 2751–2759.
- Bruker (1998). *SMART* (Version 5.0) and *SAINT* (Version 4.0). Bruker AXS Inc., Madison, Wisconsin, USA.
- Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology*. New York: Oxford University Press Inc.
- El Shaieb, K., Narayanan, V., Hopf, H., Dix, I., Fischer, A., Jones, P. G., Ernst, L. & Ibrom, K. (2003). *Eur. J. Org. Chem.* pp. 567–577.
- Flack, H. D. (1983). *Acta Cryst. A* **39**, 876–881.
- Hopf, H. & Dix, I. (2006). *Synlett*, pp. 1416–1418.
- Hopf, H., Greiving, H., Beck, C., Dix, I., Jones, P. G., Desvergne, J.-P. & Bouas-Laurent, H. (2005). *Eur. J. Org. Chem.* pp. 567–581.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Siemens (1991). *XSCANS*. Version 2.10b. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Siemens (1994). *XP*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Steiner, T. (1998). *Acta Cryst. B* **54**, 456–463.