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Three isomeric bis(methoxycarbonyl)-[2.2]paracyclophanes

Peter G. Jones,[a]* Jörg Hillmer[b] and Henning Hopf[b]

[a]Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany, and [b]Institut für Organische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany
Correspondence e-mail: jones@xray36.anchem.nat.tu-bs.de

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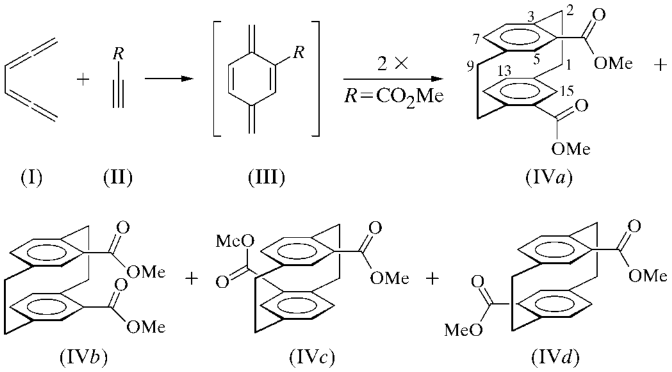
The title isomers 4,16- (pseudo-*ortho*), 4,15- (pseudo-*gem*) and 4,12-bis(methoxycarbonyl)[2.2]paracyclophane (pseudo-*para*), $C_{20}H_{20}O_4$, all show the typical structural features of [2.2]paracyclophanes (flattened boat conformation of the rings, lengthened single bonds in the bridges and narrow ring angles at the bridgehead atoms). The 4,12-isomer displays crystallographic inversion symmetry. The carbonyl groups adopt a conformation in which they are directed away from the ring systems towards the nearest bridge; the corresponding angle at the ring substituent atom is widened. Crystal packing involves C—H$\cdots\pi$ interactions for the 4,15-isomer and weak C—H$\cdots$O hydrogen bonds for the other two isomers.

Comment

When triple-bond dienophiles bearing electron-withdrawing groups are added to 1,2,4,5-hexatetraene, (I), a Diels–Alder reaction occurs, yielding a *p*-xylylene (*p*-quinodimethane) intermediate that subsequently dimerizes to a derivative of [2.2]paracyclophane (Hopf, 1972). With an unsymmetrically substituted dienophile, (II), the initial [2+4] cycloadduct is the monofunctionalized *p*-xylylene (III), which has four potential dimerization modes, yielding the isomeric disubstituted cyclophane derivatives (IV*a*)–(IV*d*) (Hopf *et al.*, 1978). We have carried out this addition with methyl propiolate for (II), *i.e.* with $R = CO_2CH_3$, and have obtained the expected mixture of isomeric bis(methoxycarbonyl)[2.2]paracyclophanes: 4,16-, (IV*a*) (the chiral pseudo-*ortho* isomer), 4,15-, (IV*b*) (pseudo-*gem*, achiral), 4,13-, (IV*c*) (pseudo-*meta*, chiral), and 4,12-, (IV*d*) (pseudo-*para*, achiral). We are interested in the structures of [2.2]paracyclophane derivatives (for recent examples, see Jones *et al.*, 2002; Focken *et al.*, 2001) and report here the structures of (IV*a*), (IV*b*) and (IV*d*); despite repeated attempts, we were unable to obtain good single crystals of (IV*c*).

All three compounds crystallize in the monoclinic system. By chance, (IV*b*) and (IV*d*) have closely similar unit-cell dimensions, although (IV*b*) has $Z' = 1$ in $P2_1$ and (IV*d*) has $Z' = \frac{1}{2}$ (inversion symmetry) in $P2_1/c$. The molecules are shown in Figs. 1–3; (IV*a*) has approximate twofold and (IV*b*) approximate mirror symmetry.



The three isomers show features typical of [2.2]paracyclophane structures. The flattened boat form of the rings is observed in each case; atoms C3, C6, C11 and C14 are displaced by 0.157 (2), 0.156 (2), 0.165 (2) and 0.161 (2) Å, respectively, for (IV*a*), and by 0.158 (3), 0.148 (3), 0.159 (3) and 0.175 (3) Å, respectively, for (IV*b*), and atoms C3 and C6 are displaced by 0.175 (2) and 0.165 (2) Å, respectively, for (IV*d*), from the plane of the remaining four ring atoms

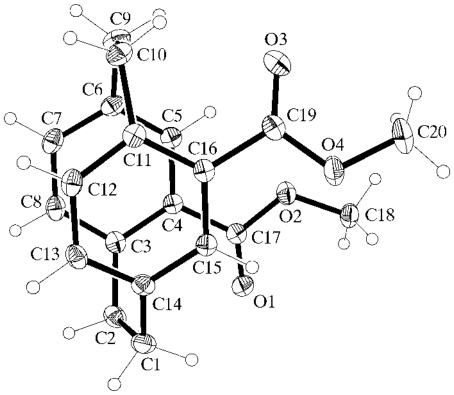


Figure 1
A view of the molecule of isomer (IV*a*) in the crystal. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

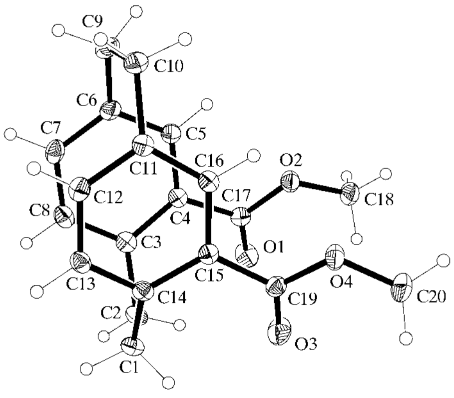


Figure 2
A view of the molecule of isomer (IV*b*) in the crystal. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

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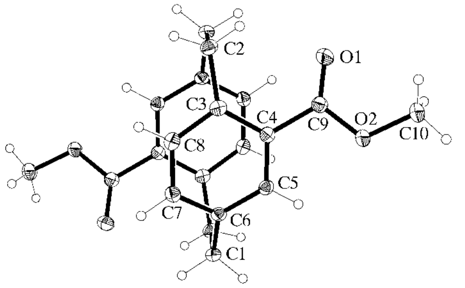

Figure 3
A view of the molecule of isomer (IV*d*) in the crystal. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

(respective mean deviations from the best planes are 0.002, 0.003, 0.008, 0.008 and 0.0004 Å). The two planes thus generated in each molecule are essentially parallel, with interplanar angles all less than 1° [zero in (IV*d*), by symmetry]. The C1—C2 and C9—C10 bridgehead bonds are lengthened to 1.588 (3) [(IV*a*), ×2], 1.590 (3) and 1.584 (3) [(IV*b*)], and 1.587 (2) Å [(IV*d*)]. The ring angles at the bridgeheads are all significantly less than 120° (Table 3).

The four non-bridgehead atoms of each ring may also be used to calculate a centroid, *Cg*; *Cg*1 is the centroid of atoms C4, C5, C7 and C8, and *Cg*2 is the centroid of atoms C12, C13, C15 and C16. Torsion angles such as C3—*Cg*1—*Cg*2—C14 show that the rings are mutually rotated by *ca* 2.5° in (IV*a*) and by 6.4° in (IV*b*); in (IV*d*), the values are zero by symmetry.

The methoxycarbonyl groups all adopt a similar conformation, in which the C═O bond is directed outwards towards the bridge [absolute C(bridgehead)—C—C═O torsion angles 16–31°] and the substituent is extended [absolute C—C—O—C(methyl) torsion angles 173–180°]. There appears to be some repulsive steric interaction between the carbonyl O atoms and the corresponding bridge regions, because the angles from the substituent-bearing C atom through the bridgehead to the bridge are all appreciably greater than 120° (Table 3). The pseudo-geminal subsitution pattern in (IV*b*) is associated with a close approach of 3.338 (3) Å between the substituent atoms C17 and C19. This relaxes to 4.109 (3) Å in pseudo-*ortho* (IV*a*).

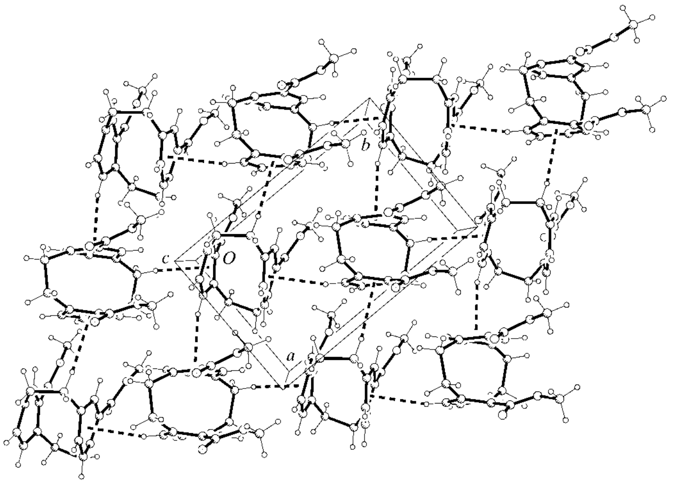

Figure 5
A packing diagram for isomer (IV*b*), viewed along the *c* axis. Weak C—H···π hydrogen bonds are indicated by dashed lines. There is one such layer per *c*-axis repeat.

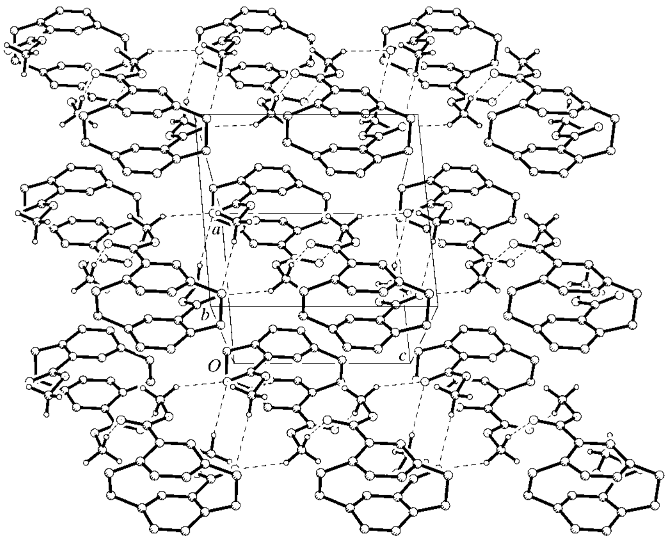

Figure 4
A packing diagram for isomer (IV*a*), viewed along the *a* axis. Non-methyl H atoms have been omitted. Weak hydrogen bonds are indicated by dashed lines.

The crystal packing of (IV*a*) (Fig. 4) involves three weak hydrogen bonds of the form C(methyl)—H···O(carbonyl) that connect the molecules into ribbons parallel to the *c* axis. The ribbons, in turn, form layers parallel to the *ac* plane, with adjacent planes being connected by a fourth weak C7—H7···O1 hydrogen bond (Table 1).

The packing of (IV*b*) involves no weak C—H···O hydrogen bonds, but the ring centroids *Cg*1 and *Cg*2 (defined as above) are involved in C8—H8···*Cg*2 (H···*Cg*2 2.72 Å and angle 167°; symmetry code: $1 - x, y - \frac{1}{2}, 1 - z$) and C10—H10*A*···*Cg*1 (H···*Cg*1 2.91 Å and angle 166°; symmetry code: $-x, \frac{1}{2} + y, 1 - z$) contacts that might be classified as C—H···π interactions. The overall effect is to connect the molecules in layers parallel to *ab* (Fig. 5).

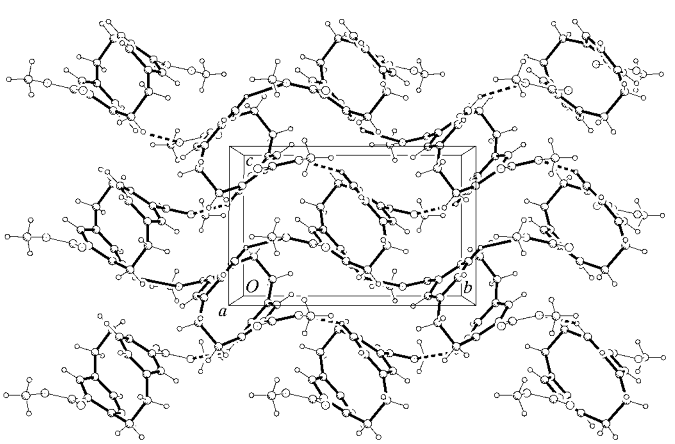

Figure 6
A packing diagram for isomer (IV*d*), viewed along the *a* axis. Weak hydrogen bonds are indicated by dashed lines. There is one such layer per *a*-axis repeat.

The packing of (IV*d*), like that of (IV*a*), is determined by C—H···O(carbonyl) interactions, which link the molecules to form layers parallel to *bc* (Fig. 6 and Table 2).

Experimental

To a solution of 1,2,4,5-hexatetraene (Hopf *et al.*, 1978), (I) (18.8 g, 0.24 mol), in diethyl ether was added methyl propiolate, (II) (16.8 g, 0.2 mol), in toluene (200 ml). The mixture was heated to 330 K for several hours while most of the ether distilled off. To complete the cycloaddition, the reaction mixture was kept at 353 K for 1 d. For work-up, the solvent was removed *in vacuo* and the oily residue taken up in dichloromethane–ethyl acetate (8:2) and passed through a silica-gel column. The prepurified product mixture (16.2 g, 25% yield) was fractionated by medium-pressure chromatography using dichloromethane–ethyl acetate (98:2, *v*/*v*) as eluant. The first fraction consisted of (IV*d*) (4.02 g, 6.2%), the second of (IV*c*) (5.19 g, 8.0%), the third of (IV*a*) (4.15 g, 6.4%) and the fourth of (IV*b*) (2.6 g, 4%). Analytically pure samples were obtained by recrystallization from chloroform. Spectroscopic and analytical data, including the separation of chiral derivatives by high-pressure liquid chromatography on optically active columns, have been described by Hillmer (1991). Single crystals were obtained by evaporation from chloroform–cyclohexane for (IV*a*) or diffusion of cyclohexane into a chloroform solution for (IV*b*) and (IV*d*).

Compound (IV*a*)

Crystal data

$C_{20}H_{20}O_4$
$M_r = 324.36$
Monoclinic, $P2_1/n$
$a = 8.096$ (4) Å
$b = 21.282$ (11) Å
$c = 9.281$ (5) Å
$\beta = 95.28$ (4)°
$V = 1592.3$ (14) Å^3
$Z = 4$

$D_x = 1.353$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 46 reflections
$\theta = 10$–12°
$\mu = 0.09$ mm^{-1}
$T = 178$ (2) K
Irregular, colourless
0.7 × 0.6 × 0.5 mm

Data collection

Nicolet *R*3 diffractometer
ω scans
2954 measured reflections
2767 independent reflections
2296 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.010$
$\theta_{\rm max} = 25°$

$h = -9 \rightarrow 9$
$k = -25 \rightarrow 0$
$l = -11 \rightarrow 1$
3 standard reflections every 147 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.119$
$S = 1.05$
2767 reflections
219 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.064P)^2 + 0.628P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.23$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.20$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °) for (IV*a*).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C18—H18*A*···O1$^{\rm i}$	0.98	2.51	3.447 (3)	160
C18—H18*B*···O3$^{\rm ii}$	0.98	2.55	3.426 (3)	149
C20—H20*A*···O3$^{\rm ii}$	0.98	2.58	3.508 (3)	157
C7—H7···O1$^{\rm iii}$	0.95	2.66	3.598 (2)	171

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8···O2$^{\rm i}$	0.95	2.63	3.438 (2)	143

Symmetry code: (i) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$.

Compound (IV*b*)

Crystal data

$C_{20}H_{20}O_4$
$M_r = 324.36$
Monoclinic, $P2_1$
$a = 7.470$ (3) Å
$b = 11.287$ (4) Å
$c = 9.494$ (3) Å
$\beta = 90.83$ (3)°
$V = 800.4$ (5) Å^3
$Z = 2$

$D_x = 1.346$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 49 reflections
$\theta = 10$–11.5°
$\mu = 0.09$ mm^{-1}
$T = 178$ (2) K
Tablet, colourless
0.45 × 0.40 × 0.20 mm

Data collection

Nicolet *R*3 diffractometer
ω scans
3864 measured reflections
1939 independent reflections
1692 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.029$
$\theta_{\rm max} = 27.5°$

$h = -6 \rightarrow 9$
$k = -10 \rightarrow 14$
$l = -12 \rightarrow 12$
3 standard reflections every 147 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.096$
$S = 1.04$
1939 reflections
219 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.054P)^2 + 0.084P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.19$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}

Table 3
Comparison of geometric parameters in (IV*a*), (IV*b*) and (IV*d*) (Å, °).

	(IV*a*)	(IV*b*)	(IV*d*)
C1—C2	1.588 (3)	1.590 (3)	1.587 (2)^a
C9—C10	1.588 (3)	1.584 (4)	
C14—C1—C2	111.75 (14)	112.82 (18)	
C1—C2—C3	112.80 (13)	111.86 (19)	112.44 (13)^b
C6—C1—C2			112.51 (12)^a
C6—C9—C10	112.29 (14)	112.77 (18)	
C9—C10—C11	112.82 (14)	112.3 (2)	
C4—C3—C8	115.95 (15)	116.5 (2)	116.23 (14)
C5—C6—C7	116.73 (16)	116.5 (2)	116.99 (14)
C12—C11—C16	116.18 (15)	116.9 (2)	
C13—C14—C15	116.68 (15)	116.7 (2)	
C2—C3—C4	124.32 (15)	122.7 (2)	125.12 (14)
C10—C11—C16	125.28 (15)		
C1—C14—C15		124.3 (2)	
C3—C4—C17—O1	16.6 (2)	30.7 (3)	
C11—C16—C19—O3	−17.1 (3)		
C14—C15—C19—O3		21.3 (4)	
C3—C4—C9—O1			−23.9 (3)
C4—C17—O2—C18	−179.12 (13)	−175.6 (2)	
C16—C19—O4—C20	173.02 (4)		
C15—C19—O4—C20		177.9 (2)	
C4—C9—O2—C10			−175.40 (14)

Notes: (*a*) atom C2 at $(1 - x, 1 - y, 1 - z)$ for (IV*d*); (*b*) atom C1 at $(1 - x, 1 - y, 1 - z)$ for (IV*d*).

Compound (IV*d*)

Crystal data

$C_{20}H_{20}O_4$
M_r = 324.36
Monoclinic, $P2_1/c$
a = 8.699 (2) Å
b = 11.790 (3) Å
c = 7.628 (2) Å
β = 91.90 (2)°
V = 781.9 (3) Å^3
Z = 2

D_x = 1.378 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 50 reflections
θ = 10–12°
μ = 0.10 mm^{-1}
T = 178 (2) K
Tablet, colourless
0.7 × 0.4 × 0.2 mm

Data collection

Nicolet R3 diffractometer
ω scans
2989 measured reflections
1789 independent reflections
1390 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.016
$\theta_{\rm max}$ = 27.5°

$h = -11 \rightarrow 11$
$k = -15 \rightarrow 0$
$l = -9 \rightarrow 9$
3 standard reflections every 147 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.131
S = 1.06
1789 reflections
110 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.064P)^2 + 0.341P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.002
$\Delta\rho_{\rm max}$ = 0.27 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.24 e Å^{-3}

Methyl H atoms were identified in difference syntheses, idealized and then refined using rigid methyl groups allowed to rotate but not tip. Other H atoms were included using a riding model. C—H bond lengths were fixed as follows: CH 0.95 Å, CH_2 0.98 Å and CH_3 0.99 Å. $U_{\rm iso}$(H) values were fixed at $1.2U_{\rm eq}$ of the parent atom. For compound (IV*b*), Friedel-opposite reflections were merged because the anomalous differences were not significant and the absolute structure could therefore not be determined.

For all compounds, data collection: *P*3 *Software* (Nicolet, 1987); cell refinement: *P*3 *Software*; data reduction: *XDISK* (Nicolet, 1987); 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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1493). Services for accessing these data are described at the back of the journal.

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