

2-15-1999

[2,3:5,6]Dibenzo[2.2.2]octa-2,5,7-triene (C₂/c)
and [2,3:5,6]dibenzo[2.2.2]octa-2,5-diene

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$S = 0.997$
 2331 reflections
 150 parameters
 H atoms treated by a
 mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0739P)^2 + 0.0414P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction:
SHELXL97 (Sheldrick,
 1997)
 Extinction coefficient:
 0.029 (5)
 Scatter factors from
*International Tables for
 Crystallography* (Vol. C)

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Table 1. Selected geometric parameters (Å, °)

O1—C2	1.195 (2)	N1—C9	1.358 (3)
O2—C2	1.342 (2)	N1—C6	1.414 (2)
O2—C3	1.415 (2)	C1—C2	1.487 (3)
O3—C9	1.222 (2)	C9—C10	1.503 (3)
C2—O2—C3	117.09 (14)	C8—C3—O2	119.17 (18)
C9—N1—C6	129.25 (17)	C7—C6—N1	117.21 (17)
O1—C2—O2	122.39 (17)	C5—C6—N1	123.69 (17)
O1—C2—C1	126.34 (18)	O3—C9—N1	123.43 (17)
O2—C2—C1	111.26 (16)	O3—C9—C10	122.37 (17)
C4—C3—O2	119.12 (17)	N1—C9—C10	114.19 (17)
C3—O2—C2—O1	−2.7 (3)	C9—N1—C6—C7	−168.3 (2)
C2—O2—C3—C4	99.8 (2)	C9—N1—C6—C5	10.3 (3)
C2—O2—C3—C8	−84.1 (2)	C6—N1—C9—O3	−4.8 (3)

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

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1N...O1 [†]	0.86 (2)	2.09 (2)	2.934 (2)	166 (1)

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

Methyl-H atoms were modelled in a riding mode and their orientations were found by refining rotation about the C—Me bonds. All other H atoms were treated isotropically. All calculations were performed on a Silicon Graphics Indy R4600.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1985). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *SAPI* (Fan, 1988). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Software used to prepare material for publication: *SHELXL97*; *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1270). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 236–239

[2,3:5,6]Dibenzo[2.2.2]octa-2,5,7-triene (C₂/c) and [2,3:5,6]dibenzo[2.2.2]octa-2,5-diene†

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Abstract

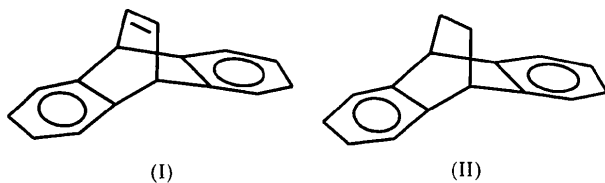
Two barrelene homologs are reported. Strain in the bicyclic framework of [2,3:5,6]dibenzo[2.2.2]octa-2,5,7-triene, (I) (C₁₆H₁₂), which is manifest in the deviations from ideality of the bond angles in the central bicyclic ring system and compression of the double bond [1.312 (3) Å], is reduced in the more saturated derivative, [2,3:5,6]dibenzo[2.2.2]octa-2,5-diene, (II) (C₁₆H₁₄), with the corresponding single bond being 1.5380 (19) Å. The formation of isomorphs of (I) in both chiral (C₂) and achiral (C₂/c) space groups has implications for asymmetric syntheses involving solid (I) which rely on a non-centrosymmetric space group.

Comment

Recent controversy concerns the origin of elongated interannular C—C single bonds in anthracene and related cycloadducts (Baldrige *et al.*, 1997). We prepared the title compounds, (I) and (II), as the first in a series of compounds designed to investigate features responsible for the anomalous bond properties in these systems. Bond distances and angles within the aromatic rings

† Alternative names: 9,10-dihydro-9,10-ethenoanthracene and 9,10-dihydro-9,10-ethanoanthracene.

of (I) and (II) were found to be fairly typical. Slight bond alternation is observed in the benzene rings, with the distal aromatic bonds (C2—C3 and C6—C7) being about 0.02 Å shorter than the proximal bonds (C4a—C9a and C8a—C10a). The double bond (C11=C12) in (I) is 1.312 (3) Å, which is relatively short for a C=C double bond. This agrees with the value of 1.316 (4) Å reported for a C2 isomorph of (I), (Ia), obtained from ethanol (Trotter & Wireko, 1990), and the value of 1.312 (3) Å for a dichloro derivative (Benites *et al.*, 1997). The corresponding single bond (C11—C12) in (II) is 1.5280 (19) Å, 0.016 Å shorter than the average of the other single bonds (C9—C12 and C10—C11) involving two C atoms with sp^3 hybridization.



Bond angles about the central bicyclic system deviate substantially from ideality. The exterior angles (C4—C4a—C10 and chemical equivalents) average 127.03° in (I) and 126.80° in (II), with the interior angles (C9a—C4a—C10 and chemical equivalents) being correspondingly smaller [averaging 112.65° in (I) and 113.09° in (II)]. The tetrahedral angles also exhibit significant distortion: C8a—C9—C9a and C4a—C10—C10a average 104.40° in (I) and 107.62° in (II), and C8a—C9—C12, C9a—C9—C12, C4a—C10—C11 and C10a—C10—C11 average 106.02° in (I) and 106.48° in (II). The angles C10—C11—C12 and C9—C12—C11 about the double bond of (I) average 114.3°, compared with 109.65° for C10—C11—C12 and C9—C12—C11 for the single bond of (II). Bond distances and angles for the two isomorphs of (I), namely, (I) and (Ia) (Trotter & Wireko, 1990), are in good agreement.

These results indicate the presence of significant strain in the bicyclic framework of (I), which is reduced in the more saturated derivative, (II). The high degree of strain in (I) is manifest most obviously in the deviations from ideality of the bond angles in the central bicyclic ring system, and compression of the C11=C12 double bond is also apparent.

Finally, the formation of a C2/c isomorph of (I) has implications for asymmetric syntheses involving solid (I) which rely on a non-centrosymmetric space group (Garcia-Garibay *et al.*, 1988). Concern that (I) and the C2 structure previously reported might be identical can be dismissed, based upon the centrosymmetric relationship between symmetry-related molecules in C2/c, which is not present in C2. Comparison of the packing of the two allotropes reveals a chiral distribution of molecules in C2. The existence of

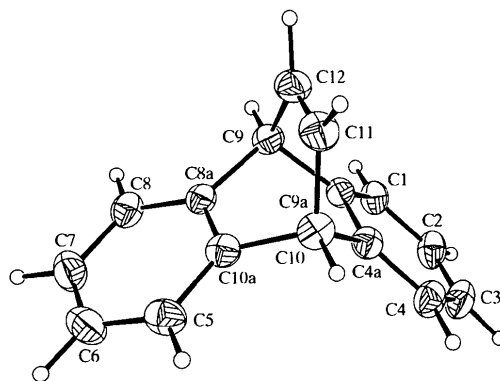


Fig. 1. ORTEP (Johnson, 1976) drawing of (I), showing the atom-labeling scheme. Displacement ellipsoids are shown at 30% probability.

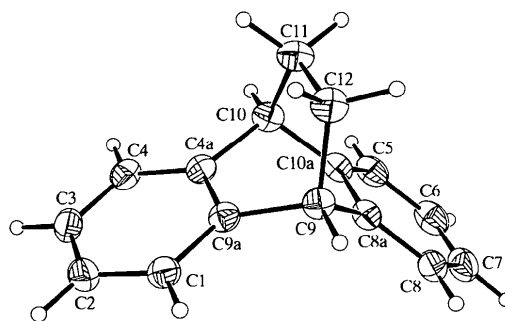


Fig. 2. ORTEP (Johnson, 1976) drawing of (II), showing the atom-labeling scheme. Displacement ellipsoids are shown at 30% probability.

centrosymmetric and non-centrosymmetric allotropes suggests that caution should be exercised in verifying the space group when attempting a chiral synthesis using crystals of this compound.

Experimental

[2,3:5,6]Dibenzo[2.2.2]octa-2,5,7-triene, (I), was prepared by Diels–Alder cycloaddition of anthracene and maleic anhydride in refluxing xylene (82% yield; Mayo *et al.*, 1989), followed by hydrolysis to the dicarboxylic acid (Cimarusti & Wolinski, 1968) and didecarboxylation with lead tetraacetate in benzene (11% yield; Miller & Stiles, 1963). The product was purified by column chromatography on activity I Woelm alumina, eluting fractionally with hexane and dichloromethane. [2,3:5,6]Dibenzo[2.2.2]octa-2,5-diene, (II), was prepared by hydrogenation of (I) at 1 atm (1 atm = 101 325 Pa) using 10% Pd/C in ethyl acetate (99% yield). Single crystals of (I) and (II) were obtained by crystallization from ethyl acetate.

Compound (I)

Crystal data

C₁₆H₁₂
M_r = 204.27

Mo K α radiation
 λ = 0.7093 Å

Monoclinic

C2/c
 $a = 14.4077$ (11) Å
 $b = 8.0758$ (7) Å
 $c = 19.0278$ (8) Å
 $\beta = 92.950$ (5)°
 $V = 2211.0$ (3) Å³
 $Z = 8$
 $D_x = 1.227$ Mg m⁻³
 D_m not measured

Data collection

Nonius CAD-4 diffractometer
 ω -scans
 Absorption correction: none
 2024 measured reflections
 1942 independent reflections
 1519 reflections with
 $I_{\text{net}} > 2\sigma(I_{\text{net}})$

Refinement

Refinement on F
 $R = 0.038$
 $wR = 0.042$
 $S = 2.06$
 1517 reflections
 146 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F) + 0.0002F^2]$
 $(\Delta/\sigma)_{\text{max}} < 0.001$

Cell parameters from 25

reflections
 $\theta = 7.8\text{--}14.3^\circ$
 $\mu = 0.069$ mm⁻¹
 $T = 293$ K
 Cube
 $0.53 \times 0.53 \times 0.53$ mm
 Colorless

$R_{\text{int}} = 0.006$
 $\theta_{\text{max}} = 25^\circ$
 $h = -17 \rightarrow 16$
 $k = 0 \rightarrow 9$
 $l = 0 \rightarrow 22$
 3 standard reflections
 frequency: 120 min
 intensity decay: none

$\Delta\rho_{\text{max}} = 0.15$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.12$ e Å⁻³
 Extinction correction:
 Larson (1970)
 Extinction coefficient:
 1.21 (12)
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

C2—C3	1.373 (3)	C9—C9a	1.527 (2)
C4a—C9a	1.397 (2)	C9—C12	1.528 (2)
C4a—C10	1.523 (2)	C10—C10a	1.520 (2)
C6—C7	1.373 (3)	C10—C11	1.523 (2)
C8a—C9	1.522 (2)	C11—C12	1.312 (3)
C8a—C10a	1.392 (2)		
C4—C4a—C10	126.95 (14)	C4a—C9a—C9	112.34 (12)
C9a—C4a—C10	112.80 (13)	C4a—C10—C10a	104.23 (11)
C8—C8a—C9	126.98 (14)	C4a—C10—C11	106.11 (13)
C9—C8a—C10a	112.68 (13)	C10a—C10—C11	106.10 (13)
C8a—C9—C9a	104.57 (12)	C5—C10a—C10	127.03 (14)
C8a—C9—C12	105.97 (12)	C8a—C10a—C10	112.79 (13)
C9a—C9—C12	105.90 (12)	C10—C11—C12	114.46 (14)
C1—C9a—C9	127.17 (13)	C9—C12—C11	114.15 (14)

Compound (II)

Crystal data

C₁₆H₁₄
 $M_r = 206.28$
 Monoclinic
 $P2_1/c$
 $a = 10.6880$ (10) Å
 $b = 6.3449$ (6) Å
 $c = 16.978$ (3) Å
 $\beta = 104.620$ (10)°
 $V = 1114.1$ (2) Å³
 $Z = 4$
 $D_x = 1.230$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.7093$ Å
 Cell parameters from 25
 reflections
 $\theta = 7.2\text{--}13.6^\circ$
 $\mu = 0.069$ mm⁻¹
 $T = 293$ K
 Plate
 $0.4 \times 0.3 \times 0.3$ mm
 Colorless

Data collection

Nonius CAD-4 diffractometer
 $R_{\text{int}} = 0.012$
 $\theta_{\text{max}} = 25^\circ$
 $h = -12 \rightarrow 12$
 $k = 0 \rightarrow 7$
 $l = 0 \rightarrow 20$
 3 standard reflections
 frequency: 120 min
 intensity decay: none

Refinement

Refinement on F
 $R = 0.035$
 $wR = 0.042$
 $S = 2.03$
 1621 reflections
 146 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F) + 0.0002F^2]$
 $(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.14$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.15$ e Å⁻³
 Extinction correction:
 Larson (1970)
 Extinction coefficient:
 1.10 (11)
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

C2—C3	1.377 (2)	C9—C9a	1.5149 (18)
C4a—C9a	1.3986 (18)	C9—C12	1.5553 (19)
C4a—C10	1.5142 (18)	C10—C10a	1.5051 (19)
C6—C7	1.380 (3)	C10—C11	1.5520 (19)
C8a—C9	1.5084 (17)	C11—C12	1.5380 (19)
C8a—C10a	1.3978 (19)		
C4—C4a—C10	126.81 (12)	C4a—C9a—C9	113.20 (11)
C9a—C4a—C10	112.84 (11)	C4a—C10—C10a	107.55 (10)
C8—C8a—C9	126.83 (12)	C4a—C10—C11	106.18 (10)
C9—C8a—C10a	112.87 (11)	C10a—C10—C11	106.84 (11)
C8a—C9—C9a	107.69 (10)	C5—C10a—C10	126.53 (12)
C8a—C9—C12	106.38 (10)	C8a—C10a—C10	113.46 (11)
C9a—C9—C12	106.50 (10)	C10—C11—C12	109.80 (11)
C1—C9a—C9	127.03 (12)	C9—C12—C11	109.50 (10)

H atoms were located by difference Fourier techniques and refined to reasonable positions during the early stages of refinement, but were fixed for the subsequent refinements.

For both compounds, data collection: *CAD-4-PC Software* (Enraf—Nonius, 1993); cell refinement: *CAD-4-PC Software*; data reduction: *DATRD2* in *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structures: *SOLVER* in *NRCVAX*; program(s) used to refine structures: *LSTSDQ* in *NRCVAX*; molecular graphics: *ORTEPII* (Johnson, 1976) in *NRCVAX*; software used to prepare material for publication: *TABLES* in *NRCVAX* (version of January 1994).

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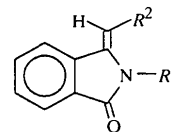
Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1160). Services for accessing these data are described at the back of the journal.

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palladium-catalyzed reaction between *N*-benzyl-*o*-iodobenzamide and phenylacetylene. We describe here the crystal structures of two additional examples, namely, (*Z*)-3-(*p*-methoxybenzylidene)isoindolin-1-one, (2), and (*Z*)-3-(2-hydroxy-2-methylpropylidene)-*N*-(*p*-tolyl)isoindolin-1-one, (3).



- (1) $R^1 = \text{CH}_2\text{Ph}$; $R^2 = \text{Ph}$
 (2) $R^1 = \text{H}$; $R^2 = \text{C}_6\text{H}_4\text{-}p\text{-OMe}$
 (3) $R^1 = \text{C}_6\text{H}_4\text{-}p\text{-Me}$; $R^2 = \text{CHC(OH)Me}_2$

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Two (*Z*)-3-aryl(alkyl)ideneisoindolin-1-ones

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Abstract

Two isoindolin-1-one derivatives, (*Z*)-3-(*p*-methoxybenzylidene)isoindolin-1-one [$\text{C}_{16}\text{H}_{13}\text{NO}_2$, (2)] and (*Z*)-3-(2-hydroxy-2-methylpropylidene)-*N*-(*p*-tolyl)isoindolin-1-one [$\text{C}_{19}\text{H}_{19}\text{NO}_2$, (3)], were synthesized by palladium-catalyzed hetero-annulation. The molecules of both compounds, which have a *Z* configuration, contain two planar parts, namely, the isoindolinone moiety and the phenyl ring. The r.m.s. deviation (0.111 Å) from the least-squares plane through the non-H atoms in compound (2) illustrates the overall molecular planarity. In (3), the phenyl ring is twisted out of the isoindolinone plane by 79.8 (1)°. Intermolecular hydrogen bonds link the molecules in (2) and (3) into infinite one-dimensional chains.

Comment

The isoindolinones (phthalamidines) form an important class of biologically important organic compounds (Fuska *et al.*, 1985) and exhibit a close structural similarity to bioactive indoles. As part of our on-going study of isoindolinone-containing heterocyclic systems of biological importance, we have reported recently the crystal structure of (*Z*)-*N*-benzyl-3-benzylideneisoindolin-1-one [(1); Khan *et al.*, 1998] prepared *via* a

The bond distances and angles observed in (2) and (3) are similar to those reported for substituted isoindoline structures (Khan *et al.*, 1998; McNab *et al.*, 1997; Barrett *et al.*, 1996; Feeder & Jones, 1996). The *Z* configurations of the molecules of (2) and (3), which contain essentially planar isoindolinone and phenyl moieties, are established by the torsion angle N—C8—C9—C10 of 0.6 (3)° in (2) and N—C7—C16—C17 of –2.7 (8)° in (3). The phenyl ring is twisted out of the isoindolinone plane (atoms C1—C8), with dihedral angles of 12.4 (1) and 79.8 (1)° in (2) and (3), respectively. The overall molecular planarity in (2) (r.m.s. deviation 0.111 Å) strongly suggests a resonance interaction extending over the C9 atom. This is reflected in a significant shortening of the C9—C10 bond length [1.437 (2) Å] in (2) compared with the C16—C17 bond [1.507 (4) Å] in (3) or with the expected $\text{C}_{\text{aryl}}\text{—C}_{\text{sp}^2}$ distance. The exocyclic bond angles around atoms C8 [in (2)] and C7 [in (3)] are highly asymmetric, with the N—C8—C9 [in (2)] and N—C7—C16 [in (3)] angles being markedly larger than the other angles. Intermolecular hydrogen bonds [N—

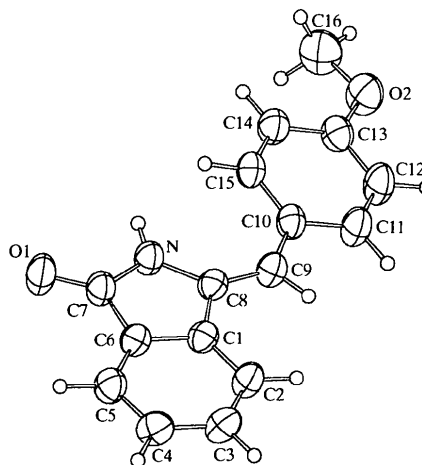


Fig. 1. ORTEPII (Johnson, 1976) view (50% probability level) of (2).