N2—C17	1.388 (5)	N22—C37	1.389 (5)
N2—C13	1.469 (4)	N22—C33	1.469 (5)
C1—C2	1.479 (5)	C21—C22	1.481 (5)
C2—C3	1.329 (5)	C22—C23	1.324 (5)
C3—C4	1.474 (5)	C23—C24	1.465 (5)
C14—C15	1.523 (6)	C34—C35	1.537 (6)
C15—C16	1.530 (6)	C35—C36	1.535 (6)
C15—C18	1.428 (6)	C35—C38	1.452 (6)
C14—C15—C16	103.6 (4)	C34—C35—C36	102.0 (3)
C2—C3—C4—C5	−7.3 (6)	C22—C23—C24—C25	13.9 (6)
C1—N1—C10—C11	−92.0 (4)	C21—N21—C30—C31	−91.8 (4)
C14—N2—C13—C12	89.1 (5)	C34—N22—C33—C32	82.7 (4)

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

D—H···A	D—H	H···A	D···A	D—H···A
O7—H7···O1'	0.89 (4)	1.83 (4)	2.679 (4)	160 (4)
N1—H1···O34"	0.81 (4)	2.31 (4)	3.078 (4)	160 (4)
O27—H27···O21'"	0.90 (5)	1.78 (5)	2.671 (4)	173 (4)
N21—H21···O14"	0.81 (4)	2.18 (4)	2.971 (4)	168 (3)

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

The *BUNYIP* program (Hester & Hall, 1995) indicated that the two independent molecules in the asymmetric unit are closely related by a centre of inversion. Tests for overlooked super-lattice reflections and transformations of the unit-cell parameters confirmed that additional crystallographic symmetry is not present. All H atoms were initially located in a difference electron-density map. The positions and isotropic displacement parameters of those attached to N and O atoms were refined freely. The positions of the H atoms bonded to C atoms were geometrically optimized and allowed to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. Methyl groups were treated as rotating rigid groups with $U_{iso}(H) = 1.5U_{eq}(C)$. A total of 304 reflections with $F_o^2 < -2\sigma(F_o^2)$ were excluded during refinement.

The two largest peaks of residual electron density (0.73 and 0.59 e Å^{-3}) are located within 1.1 Å of C15 and C35 and their positions suggest conformational disorder of the five-membered ring in each independent molecule. Attempts to refine C15 and C35 as disordered atoms, even with bond-length and similarity restraints, produced unsatisfactory results. The unusually short bond lengths for C15—C18 and C25—C38 are probably the result of the inadequately modelled disorder.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS86* direct methods (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Photoproducts Derived from 9-Substituted Dibenzobarrelenes

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Abstract

Irradiation of 11,12-dibenzoyl-9,10-dihydro-9-hydroxy-methyl-9,10-ethenoanthracene, (1a), and 11,12-dibenzoyl-9,10-dihydro-9-methoxy-9,10-ethenoanthracene, (1b),

gave the corresponding 4b-substituted dibenzosemibull-valenes, 8c,8d-dibenzoyl-4b-hydroxymethyl-4b,8b,8c,8d-tetrahydrodibenzo[a,f]cyclopropa[cd]pentalene, $C_{31}H_{22}$-O_3, (2a), and 8c,8d-dibenzoyl-4b-methoxy-4b,8b,8c,8d-tetrahydrodibenzo[a,f]cyclopropa[cd]pentalene, $C_{31}H_{22}$-O_3, (2b), respectively. The molecular structures of (2a) and (2b) have been established unambiguously by single-crystal X-ray diffraction studies.

Comment

The triplet-state mediated rearrangements of dibenzobar-relenes, in general, lead to the corresponding dibenzo-semibullvalenes (Ciganek, 1966; Rabideau, Hamilton & Friedman, 1968; Zimmerman, 1980, 1991; Scheffer & Yang, 1995). In earlier studies, we reported the photo-transformations of several dibenzobarrelenes each con-taining a 1,2-dibenzoylalkene moiety (Kumar, Murty, Lahiri, Chakachery, Scaiano & George, 1984; Murty, Pratapan, Kumar, Das & George, 1985; Pratapan, Ashok, Gopidas, Rath & George, 1990; Asokan, Kumar, Das, Rath & George, 1991; Ajayakumar, Asokan, Das, Wilbur, Rath & George, 1993; Ramaiah, Ku-mar, Asokan, Mathew, Das, Rath & George, 1996). It has been observed that, in general, they undergo photorearrangement, leading primarily to dibenzo-semibullvalenes or products derived from them. When the dibenzobarrelenes have bridgehead substituents, then regioisomeric dibenzosemibullvalenes could result. The regioselectivity in these rearrangements could, however, depend on several factors, including both steric and elec-tronic requirements of the bridgehead substituents.

In earlier studies, we reported, on the basis of analyti-cal results and spectral data, that the 9-hydroxymethyl-substituted dibenzobarrelene (1a) (Pratapan, Ashok, Cyr, Das & George, 1987) and the 9-methoxy-substituted dibenzobarrelene (1b) (Murty et al., 1985), on irra-diation, give the corresponding 4b-substituted diben-zosemibullvalenes (2a) and (2b), respectively. In order to assess the effects of the bridgehead substituents in the starting dibenzobarrelenes on the observed regioselec-tivity in their photoproducts, the structures of both (2a) and (2b) have been determined unambiguously through X-ray crystallographic analysis. In both cases, the sub-stituents originally present at the C9 positions of the starting dibenzobarrelenes have ended up at the 4b positions of the dibenzosemibullvalenes.
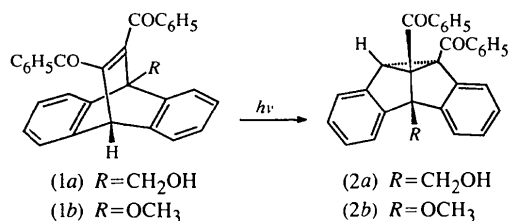
The molecular structure of each compound contains a 6,5,3,5,6-fused ring system, shaped like a butterfly with wings hanging down from two sides of the C4b—C8c bond. The 'butterfly angles' formed by the fusion of the two indane ring systems are 88.68 (4) and 89.58 (3)° for (2a) and (2b), respectively. The structures show geometric parameters within the accepted range.

Both compounds (2a) and (2b) have good hydrogen-bond acceptors. However, only (2a) has a hydrogen-bond donor, the OH group. In spite of this important difference, the molecules are structural isomers (Figs. 1 and 2 show projection views of the molecules in similar orientations, with displacement ellipsoids drawn at the same probability level).
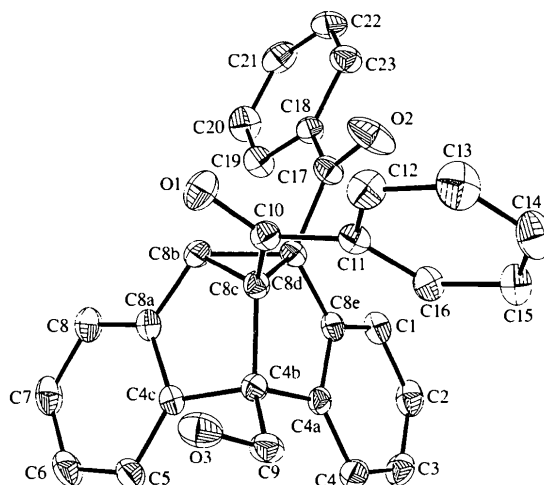

Fig. 1. A view of the molecule of (2a) showing the labelling of the non-H atoms. Displacement ellipsoids are drawn at the 30% probability level.
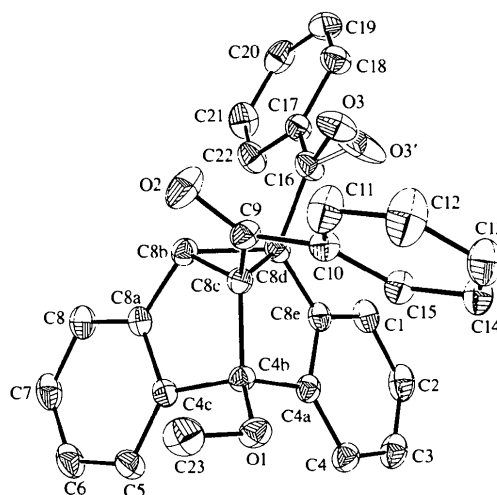

Fig. 2. A view of the molecule of (2b) showing the labelling of the non-H atoms. Displacement ellipsoids are drawn at the 30% probability level.

(1a) R=CH₂OH
(1b) R=OCH₃

(2a) R=CH₂OH
(2b) R=OCH₃

The packing diagrams of the two molecules (Figs. 3 and 4) show the differences in their crystal-packing environments. In the case of (2a), intermolecular hydrogen bonding is observed between the hydroxyl H atom and the carbonyl O atom of a neighbouring molecule [H3—O1^i 2.06 (8) Å and O3—H3· · ·O1^i 170 (1)°; symmetry code: (i) $1 - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$]. No hydrogen bonding was observed for (2b). Since the unit-cell contents are the same for both structures, as expected, the less dense of the two, (2b) [d_{calc} = 1.320 and 1.289 Mg m^{-3} for (2a) and (2b), respectively], has a higher average U_{eq} [52 and 57 Å^2 × 10^3 for (2a) and (2b), respectively].
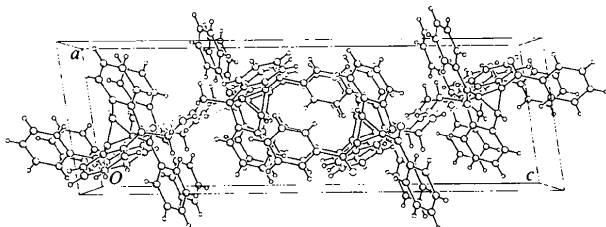

Fig. 3. Molecular packing of (2a) with intermolecular hydrogen bonds.
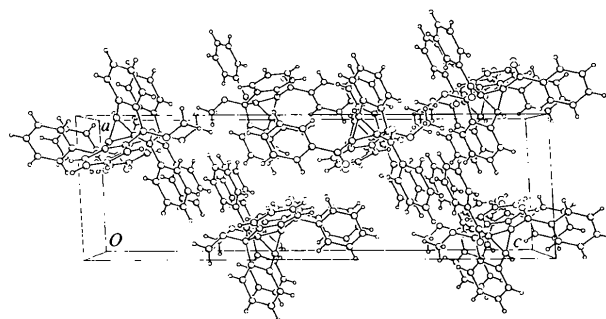

Fig. 4. Crystal packing of (2b).

Experimental

Compounds (2a) and (2b) were crystallized from a 1:1 mixture of benzene/petroleum ether and methylene chloride/methanol, respectively, according to Murty *et al.* (1985).

Compound (2a)

Crystal data

C$_{31}$H$_{22}$O$_3$
M_r = 442.49
Monoclinic
$P2_1/c$
a = 8.8144 (1) Å
b = 9.1481 (1) Å
c = 27.8748 (3) Å
β = 97.827 (1)°
V = 2226.74 (4) Å^3
Z = 4
D_x = 1.320 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 8192 reflections
θ = 2.0–18.0°
μ = 0.084 mm^{-1}
T = 298 (2) K
Irregular
0.30 × 0.30 × 0.20 mm
Colourless

Data collection

Siemens SMART diffractometer
ω scans
Absorption correction: none
15746 measured reflections
4380 independent reflections

2896 reflections with
$I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 26.0°
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -38 \rightarrow 38$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.128
S = 1.01
4319 reflections
311 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0495P)^2 + 0.7533P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: none
Scattering factors from
  International Tables for Crystallography (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (2a)*

C4a—C8e	1.394 (3)	C8a—C8b	1.475 (3)
C4a—C4b	1.535 (3)	C8b—C8c	1.508 (3)
C4b—C4c	1.534 (3)	C8b—C8d	1.556 (3)
C4b—C8c	1.576 (3)	C8c—C8d	1.524 (2)
C4c—C8a	1.388 (3)	C8d—C8e	1.492 (3)
C8e—C4a—C4b	110.3 (2)	C8c—C8b—C8d	59.62 (12)
C4c—C4b—C4a	102.48 (15)	C8b—C8c—C8d	61.77 (12)
C4c—C4b—C8c	102.81 (15)	C8b—C8c—C4b	104.13 (15)
C4a—C4b—C8c	102.69 (14)	C8d—C8c –C4b	104.82 (14)
C8a—C4c—C4b	110.1 (2)	C8c—C8d—C8e	106.99 (15)
C4c—C8a—C8b	109.9 (2)	C8c—C8d—C8b	120.1 (2)
C8—C8a—C8b	129.3 (2)	C8c—C8d—C8b	58.61 (12)
C8a—C8b—C8c	108.6 (2)	C4a—C8e—C8d	110.3 (2)
C8a—C8b—C8d	120.1 (2)		

Compound (2b)

Crystal data

C$_{31}$H$_{22}$O$_3$
M_r = 442.49
Monoclinic
$P2_1/c$
a = 8.7753 (1) Å
b = 9.2567 (1) Å
c = 28.1011 (2) Å
β = 92.934 (1)°
V = 2279.67 (4) Å^3
Z = 4
D_x = 1.289 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 8192 reflections
θ = 2.0–18.0°
μ = 0.082 mm^{-1}
T = 298 (2) K
Rectangular
0.42 × 0.28 × 0.28 mm
Colourless

Data collection

Siemens SMART diffractometer
ω scans
Absorption correction: none
17324 measured reflections
4494 independent reflections

3415 reflections with
$I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 26.0°
$h = -12 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = -38 \rightarrow 38$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.118$
$S = 1.06$
4484 reflections
317 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.046P)^2 + 0.7746P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C4a—C8e	1.391 (2)	C8a—C8b	1.474 (2)
C4a—C4b	1.516 (2)	C8b—C8c	1.501 (2)
C4b—C4c	1.532 (2)	C8b—C8d	1.559 (2)
C4b—C8c	1.580 (2)	C8c—C8d	1.517 (2)
C4c—C8a	1.384 (2)	C8d—C8e	1.492 (2)
C4—C4a—C4b	128.6 (2)	C8c—C8b—C8d	59.39 (10)
C8e—C4a—C4b	109.79 (14)	C8b—C8c—C8d	62.22 (11)
C4a—C4b—C4c	103.50 (13)	C8b—C8c—C4b	104.10 (13)
C4a—C4b—C8c	103.42 (13)	C8d—C8c—C4b	103.81 (13)
C4c—C4b—C8c	102.80 (13)	C8c—C8d—C8c	107.14 (14)
C8a—C4c—C4b	110.18 (14)	C8e—C8d—C8b	121.01 (14)
C4c—C8a—C8b	110.09 (14)	C8c—C8d—C8b	58.39 (10)
C8a—C8b—C8c	108.51 (14)	C4a—C8e—C8d	110.35 (14)
C8a—C8b—C8d	120.03 (15)		

Data were collected by the double-pass method using a charge-coupled device area-detector system. The first 50 frames of data were recollected at the end of data collection to monitor crystal decay. The structures were solved by direct methods and refined successfully in the monoclinic space group $P2_1/c$. Full-matrix least-squares refinement was carried out by minimizing $w(F_o^2 - F_c^2)^2$. The non-H atoms were refined anisotropically to convergence. The H atoms were treated using appropriate riding models (*AFIX* = m3; *SHELXTL-Plus*; Sheldrick, 1995), except for the hydroxyl H atom of (2a) which was refined freely with an isotropic displacement parameter. One of the carbonyl O atoms (O3) in compound (2b) exhibits disorder, with two positions O3 and O3' which are 0.23 (1) Å above and below the mean plane defined by atoms C8d, C16 and C17 and the midpoint of O3 and O3'. The refined occupancy factor for O3 is 0.58 (5).

For both compounds, data collection: *SMART* software (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structures: *SHELXTL-Plus* (Sheldrick, 1995); program(s) used to refine structures: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELX-Plus*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1278). Services for accessing these data are described at the back of the journal.

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Tyrosinium-D-tetrahydroisoquinoline-3-carboxylate 1.5-Hydrate and Tyrosyl-D-tetrahydroisoquinoline-3-carboxamide Hydrate

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Abstract

Crystals of the two dipeptide title compounds, Tyr-D-Tic, $C_{19}H_{20}N_2O_4 \cdot 1.5H_2O$, and Tyr-D-Tic-NH$_2$, $C_{19}H_{21}N_3O_3 \cdot H_2O$, were prepared by the sitting-drop method. Tyr-D-Tic is orthorhombic ($P2_12_12_1$) and crystallizes as a zwitterion. The asymmetric unit contains two peptide molecules and three molecules of water.