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Structure of an Optically Active Anthracycline Precursor

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Abstract

The crystal structure of (1*S*,3*S*)-3-acetyl-5-methoxy-3-methylthio-1,2,3,4-tetrahydronaphthalene-1,8-diyl dibenzoate contains two independent molecules. These molecules have a similar conformation except for the dihedral angles between the aromatic ring and the benzoyloxy group linked to it, which differ by a relative rotation of −160°. The absolute configurations of the two chiral centres C8 and C10 are established as *S* and *S*.

Comment

The compound was synthesized as a precursor of optically pure anthracyclines. The structure determination of the compound was undertaken to confirm the absolute configurations of the two chiral centres, which were established as *S* and *S*. The C10 chiral centre was constructed *via* chirality-transferred ene reaction (Tanino, Shoda, Nakamura & Kuwajima, 1992), and the cyclohexane ring cyclization reaction between C7 and C8 afforded a single diastereomer. Details of the synthetic work will be published elsewhere (Adachi, Masuya, Tanino & Kuwajima, 1993).

The structure contains two independent $C_{28}H_{26}O_6S$ molecules which have similar conformations. The cyclohexane ring in each molecule adopts a half-chair conformation with an axial acetyl group and an equatorial methylthio group. The benzoyloxy group linked to the cyclohexane ring at C10 is in an equatorial position. The main difference between the two molecules is in the conformation of the benzoyloxy group at C2. The dihedral angles C1*A*—C2*A*—O3*A*—C15*A* and C1*B*—C2*B*—O3*B*—C15*B* are 84.8 (4) and −115.2 (4)°, respectively.

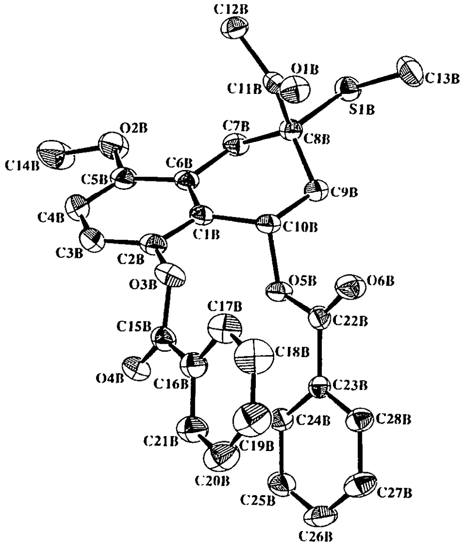

Fig. 1. A perspective view of molecule *B* with numbering scheme, excluding H atoms (30% probability ellipsoids).

Experimental

Crystal data

$C_{28}H_{26}O_6S$
M_r = 490.570
Triclinic
$P1$
a = 10.159 (2) Å
b = 13.533 (5) Å
c = 10.016 (3) Å
α = 108.10 (2)°
β = 102.92 (2)°
γ = 96.30 (2)°
V = 1251.5 (7) Å^3
Z = 2
D_x = 1.302 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.54184 Å
Cell parameters from 25 reflections
θ = 27.33–27.45°
μ = 1.447 mm^{-1}
T = 296.15 K
Prism
0.80 × 0.35 × 0.30 mm
Colourless
Crystal source: recrystallization from ethanol

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Data collection

Rigaku AFC-5*R* four-circle diffractometer
Profile data from $\theta/2\theta$ scans
Absorption correction: none
7825 measured reflections
3914 independent reflections
6822 observed reflections [$F > 3.0\sigma(F)$]

$R_{\rm int} = 2.7$
$\theta_{\rm max} = 62.0°$
$h = -11 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = -11 \rightarrow 11$
3 standard reflections monitored every 100 reflections intensity variation: none

Refinement

Refinement on *F*
Final $R = 0.0425$
$wR = 0.0556$
$S = 2.45$
6822 reflections
628 parameters
H atoms calculated; not refined

$w^{-1} = \sigma(F_o)^2$
$(\Delta/\sigma)_{\rm max} = 0.03$
$\Delta\rho_{\rm max} = 0.30$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.36$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Data collection: *AFC*-5 software (Molecular Structure Corporation, 1985). Cell refinement: *AFC*-5 software. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1986). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1985). Molecular graphics: *ORTEP*II (Johnson, 1976).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
Molecule *A*				
S1	0.5994	0.3421	0.7544	0.0491
O1	0.7684 (3)	0.5572 (2)	1.0719 (3)	0.0634
O2	0.6828 (3)	0.6440 (2)	0.5481 (3)	0.0593
O3	0.5333 (2)	0.8608 (2)	1.0389 (2)	0.0459
O4	0.7356 (3)	0.8730 (3)	1.1939 (3)	0.0808
O5	0.3721 (2)	0.6576 (2)	0.9512 (2)	0.0429
O6	0.3963 (3)	0.6894 (3)	1.1897 (3)	0.0713
C1	0.5702 (3)	0.6966 (2)	0.8770 (3)	0.0366
C2	0.5782 (3)	0.8060 (3)	0.9179 (3)	0.0424
C3	0.6228 (3)	0.8631 (3)	0.8387 (4)	0.0489
C4	0.6579 (4)	0.8107 (3)	0.7130 (4)	0.0491
C5	0.6521 (3)	0.7032 (3)	0.6706 (3)	0.0433
C6	0.6091 (3)	0.6443 (3)	0.7533 (3)	0.0398
C7	0.6032 (3)	0.5265 (3)	0.7035 (3)	0.0420
C8	0.6166 (3)	0.4865 (2)	0.8336 (3)	0.0376
C9	0.5007 (3)	0.5165 (3)	0.9022 (3)	0.0436
C10	0.5117 (3)	0.6371 (2)	0.9627 (3)	0.0390
C11	0.7580 (3)	0.5268 (2)	0.9425 (3)	0.0404
C12	0.8824 (3)	0.5240 (3)	0.8857 (4)	0.0589
C13	0.6228 (4)	0.3019 (3)	0.9122 (5)	0.0689
C14	0.7024 (5)	0.6940 (4)	0.4454 (4)	0.0766
C15	0.6227 (3)	0.8923 (3)	1.1742 (4)	0.0471
C16	0.5633 (3)	0.9503 (2)	1.2893 (3)	0.0428
C17	0.4314 (4)	0.9707 (3)	1.2600 (4)	0.0565
C18	0.3817 (4)	1.0258 (3)	1.3739 (5)	0.0709
C19	0.4635 (5)	1.0613 (3)	1.5145 (5)	0.0706
C20	0.5930 (5)	1.0410 (3)	1.5444 (4)	0.0719
C21	0.6437 (4)	0.9865 (3)	1.4326 (4)	0.0590
C22	0.3326 (3)	0.6905 (3)	1.0736 (3)	0.0413
C23	0.2039 (3)	0.7331 (2)	1.0486 (3)	0.0403
C24	0.1503 (3)	0.7511 (3)	0.9209 (4)	0.0458
C25	0.0320 (4)	0.7932 (3)	0.9036 (4)	0.0587
C26	−0.0328 (4)	0.8166 (3)	1.0143 (5)	0.0670
C27	0.0203 (4)	0.7987 (3)	1.1413 (5)	0.0686
C28	0.1371 (3)	0.7558 (3)	1.1587 (4)	0.0542
Molecule *B*				
S1	0.11282 (12)	0.66448 (8)	0.47780 (12)	0.0510
O1	0.2556 (3)	0.4474 (2)	0.5005 (3)	0.0595
O2	−0.3277 (3)	0.3807 (2)	0.3578 (3)	0.0716
O3	0.0031 (3)	0.1424 (2)	0.0805 (3)	0.0577
O4	−0.1551 (3)	0.0756 (2)	−0.1378 (3)	0.0663
O5	0.0551 (2)	0.3326 (2)	0.0251 (2)	0.0461
O6	0.2807 (3)	0.3433 (3)	0.0409 (3)	0.0669
C1	−0.0454 (3)	0.3095 (2)	0.2057 (3)	0.0415
C2	−0.0874 (3)	0.1991 (3)	0.1454 (3)	0.0493
C3	−0.2062 (4)	0.1484 (3)	0.1579 (4)	0.0610
C4	−0.2886 (4)	0.2065 (3)	0.2273 (4)	0.0653
C5	−0.2506 (3)	0.3157 (3)	0.2885 (4)	0.0536
C6	−0.1264 (3)	0.3687 (3)	0.2820 (3)	0.0433
C7	−0.0819 (3)	0.4869 (3)	0.3565 (3)	0.0457
C8	0.0746 (3)	0.5190 (2)	0.3935 (3)	0.0389
C9	0.1178 (3)	0.4818 (3)	0.2536 (3)	0.0470
C10	0.0837 (3)	0.3612 (3)	0.1843 (3)	0.0418
C11	0.1513 (3)	0.4798 (2)	0.5104 (3)	0.0417
C12	0.0970 (4)	0.4864 (3)	0.6394 (3)	0.0531
C13	0.2986 (4)	0.6955 (3)	0.5217 (5)	0.0695
C14	−0.4686 (4)	0.3384 (5)	0.3366 (5)	0.1036
C15	−0.0387 (4)	0.0882 (3)	−0.0656 (4)	0.0521
C16	0.0760 (4)	0.0492 (3)	−0.1214 (4)	0.0568
C17	0.2090 (5)	0.0672 (3)	−0.0329 (5)	0.0712
C18	0.3119 (6)	0.0324 (5)	−0.0927 (6)	0.0934
C19	0.2859 (7)	−0.0218 (4)	−0.2385 (7)	0.0946
C20	0.1554 (7)	−0.0401 (4)	−0.3281 (6)	0.0896
C21	0.0492 (5)	−0.0044 (3)	−0.2698 (5)	0.0712
C22	0.1636 (3)	0.3219 (2)	−0.0323 (3)	0.0421
C23	0.1181 (3)	0.2784 (2)	−0.1935 (3)	0.0397
C24	−0.0202 (3)	0.2518 (3)	−0.2726 (3)	0.0486
C25	−0.0561 (4)	0.2087 (3)	−0.4222 (4)	0.0652
C26	0.0445 (5)	0.1926 (3)	−0.4944 (4)	0.0716
C27	0.1823 (5)	0.2218 (3)	−0.4178 (4)	0.0649
C28	0.2187 (4)	0.2638 (3)	−0.2677 (4)	0.0521

Table 2. *Geometric parameters* (Å, °)

Molecule *A*		Molecule *B*	
S1—C8	1.839 (3)	S1—C8	1.842 (3)
S1—C13	1.801 (5)	S1—C13	1.809 (4)
O1—C11	1.207 (4)	O1—C11	1.203 (4)
C1—C6	1.388 (4)	C1—C6	1.396 (5)
C1—C10	1.515 (5)	C1—C10	1.507 (5)
C6—C7	1.504 (5)	C6—C7	1.506 (4)
C7—C8	1.544 (5)	C7—C8	1.529 (4)
C8—C9	1.522 (5)	C8—C9	1.515 (5)
C8—C11	1.519 (4)	C8—C11	1.526 (5)
C9—C10	1.536 (5)	C9—C10	1.526 (5)
C11—C12	1.497 (5)	C11—C12	1.497 (5)
C8—S1—C13	102.9 (2)	C8—S1—C13	102.7 (2)
C6—C1—C10	121.5 (3)	C6—C1—C10	121.9 (3)
C1—C6—C7	121.6 (3)	C1—C6—C7	120.9 (3)
C6—C7—C8	110.6 (2)	C6—C7—C8	110.4 (3)
S1—C8—C7	105.4 (2)	S1—C8—C7	105.5 (2)
S1—C8—C9	111.9 (2)	S1—C8—C9	112.1 (2)
S1—C8—C11	106.0 (2)	S1—C8—C11	104.0 (2)
C7—C8—C9	107.6 (3)	C7—C8—C9	108.5 (2)
C7—C8—C11	112.8 (3)	C7—C8—C11	113.2 (3)
C9—C8—C11	113.0 (2)	C9—C8—C11	112.4 (3)
C8—C9—C10	111.9 (3)	C8--C9—C10	111.3 (3)
C1—C10—C9	114.6 (3)	C1—C10—C9	114.6 (3)
O1—C11—C8	120.0 (3)	O1—C11—C8	120.2 (3)
O1—C11—C12	121.4 (3)	O1—C11—C12	121.1 (3)
C8—C11—C12	118.6 (3)	C8—C11—C12	118.6 (3)
C13—S1—C8—C7	177.8 (2)	C13—S1—C8—C7	178.7 (2)
C13—S1—C8—C9	−65.5 (3)	C13—S1—C8—C9	−63.3 (3)
C13—S1—C8—C11	58.0 (3)	C13—S1—C8—C11	58.9 (3)
C15—O3—C2—C1	84.8 (4)	C15—O3—C2—C1	−115.2 (4)
C15—O3—C2—C3	−98.5 (4)	C15—O3—C2—C3	69.2 (4)
C22—O5—C10—C1	−130.1 (3)	C22—O5—C10—C1	−149.2 (3)
C22—O5—C10—C9	107.5 (3)	C22—O5—C10—C9	88.3 (3)
C6—C7—C8—S1	177.4 (2)	C6—C7—C8—S1	178.2 (2)
C6—C7—C8—C9	57.9 (3)	C6—C7—C8—C9	57.9 (3)
C6—C7—C8—C11	−67.4 (3)	C6—C7—C8—C11	−67.6 (4)

S1—C8—C9—C10	−177.6 (2)	S1—C8—C9—C10	−179.3 (2)
C7—C8—C9—C10	−62.4 (3)	C7—C8—C9—C10	−63.2 (3)
C11—C8—C9—C10	62.9 (4)	C11—C8—C9—C10	62.8 (4)
S1—C8—C11—O1	−107.5 (3)	S1—C8—C11—O1	−104.8 (3)
S1—C8—C11—C12	70.2 (3)	S1—C8—C11—C12	72.9 (3)
C7—C8—C11—O1	137.6 (3)	C7—C8—C11—O1	140.7 (3)
C7—C8—C11—C12	−44.6 (4)	C7—C8—C11—C12	−41.6 (4)
C9—C8—C11—O1	15.3 (4)	C9—C8—C11—O1	17.3 (4)
C9—C8—C11—C12	−167.0 (3)	C9—C8—C11—C12	−165.0 (3)

Reflections were measured for whole space to determine the absolute configuration. The structure was refined for two configurations: R = 0.054 and wR = 0.072 for the R modification; R = 0.043 and wR = 0.056 for the S modification. The absolute configuration was assigned from the enantiomeric structure which refined with the lower R value.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71094 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1040]

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Structures of α-Phenyl-amino-stilbene Derivatives

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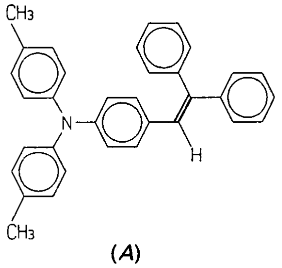
Abstract

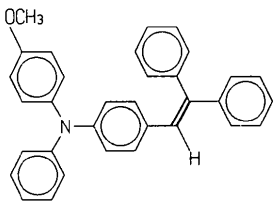
The crystal structures of two α-phenyl-amino-stilbene derivatives have been determined: (*A*) α-phenyl-4′-[bis(4-methylphenyl)amino]stilbene; (*B*) α-phenyl-4′-[(4-methoxyphenyl)phenylamino]stilbene. Compound (*A*) consists of two crystallographically independent molecules A and A'. The geometrical difference between molecules A and A' lies mainly in the distortion between the two benzene rings of the *trans*-stilbene moiety. The *trans*-stilbene moiety in compound (*B*) is approximately planar, while those in the molecules A and A' are not. Nevertheless, the planarity of the molecules A and A', as a whole, is better than that of compound (*B*). The molecules in (*A*) are arranged on the *ac* plane in such a way that the directions of the *trans*-stilbene moiety are almost parallel and are stacked along the *b* axis. Planes of the *trans*-stilbene moiety in (*B*) are parallel; the anisole-group planes are nearly perpendicular to these planes.

Comment

The structures of the title compounds were determined as part of studies on charge-transport materials. The C(8)—C(31) and C(8)—C(41) bond lengths observed in these compounds are longer than the corresponding distances in *trans*-bis(4-dimethylaminonaphthalene-1-azo)-4,4′-stilbene [1.458 (3) Å (Foitzik, Paulus, Haase & Loub, 1991)]. The angle C(4)—C(7)—C(8) is larger and the angles C(7)—C(8)—C(31) and C(7)—C(8)—C(41) are smaller than the corresponding angles in *trans*-bis(4-dimethylaminonaphthalene-1-azo)-4,4′-stilbene [127.1 (2), 127.5 (2)° (Foitzik, Paulus, Haase & Loub, 1991)]. They are the result of the repulsion between the two phenyl groups bonded to the α-C atom.



(*A*)



(*B*)

The dihedral angle between the two *trans*-stilbene benzene rings in (*B*) [25.0 (2)°] is much smaller than those in (*A*) [60.1 (2) and 77.0 (2)° in molecules A and A', respectively]. Therefore, the *trans*-stilbene moiety in (*B*) is approximately planar, while those in (*A*) are not. The plane N(1)-C(1)-C(11)-C(21) and the plane C(7)-C(8)-C(31)-C(41) in molecules A and A' of compound (*A*) are inclined in the same direction with respect to the plane formed by the C(1)-C(6) ring; but those in (*B*) are inclined in the opposite direction. The dihedral angles between the plane N(1)-C(1)-C(11)-C(21) and the plane C(7)-C(8)-C(31)-C(41) in molecules A and A' are small [10.2 (3) and 2.9 (3)°, respectively], while that in (*B*) is as large

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