

$\theta/2\theta$  scans  $h = -14 \rightarrow 14$   
 Absorption correction: none  $k = 0 \rightarrow 29$   
 6324 measured reflections  $l = 0 \rightarrow 14$   
 5999 independent reflections 2 standard reflections  
 4431 reflections with every 50 reflections  
 $I > 2\sigma(I)$  intensity decay: 8%

**Refinement**

Refinement on  $F$   $\Delta\rho_{\max} = 0.67 (6) \text{ e } \text{\AA}^{-3}$   
 $R = 0.057$   $\Delta\rho_{\min} = -0.39 (6) \text{ e } \text{\AA}^{-3}$   
 $wR = 0.067$  Extinction correction: type 1,  
 $S = 1.466$  Lorentzian isotropic  
 4431 reflections (Becker & Coppens,  
 508 parameters 1975); mean path length  
 H-atom parameters put to 1  
 constrained Extinction coefficient:  
 $w = 1/[\{\sigma(F^2) + 1.03F^2\}^{1/2}$   $4 (4) \times 10$   
 $- |F|^2]$  Scattering factors from *Inter-*  
 $(\Delta/\sigma)_{\max} = 0.004$  *national Tables for X-ray*  
*Crystallography* (Vol. IV)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

S1—C5	1.780 (4)	O2—C26	1.390 (5)
S1—C29	1.790 (5)	O2—C36	1.434 (5)
S2—C11	1.772 (4)	C1—C2	1.532 (5)
S2—C30	1.790 (5)	C2—C3	1.500 (6)
O1—C25	1.369 (5)	C7—C8	1.513 (6)
O1—C33a	1.453 (14)	C8—C9	1.531 (5)
O1—C33b	1.481 (10)		
C24—C1—C2—C3	51.2 (5)	C12—C13—C14—C15	57.6 (5)
C1—C2—C3—C4	-112.2 (4)	C13—C14—C15—C16	-99.0 (4)
C6—C7—C8—C9	111.7 (4)	C18—C19—C20—C21	100.6 (4)
C7—C8—C9—C10	-61.0 (5)	C19—C20—C21—C22	-51.3 (5)

Data collection was performed at 120 K by means of a Huber four-circle diffractometer equipped with an Oxford Cryosystems Cryostream unit (Cosier & Glazer, 1986). The unit-cell dimensions were determined from reflections measured at  $\pm 2\theta$ . Data were corrected for background, Lorentz and polarization effects. The positions of H atoms were calculated. Non-H atoms were refined anisotropically. The propoxy groups attached to the two phenyl groups inclined to the axis of the molecule exhibit a twofold disorder. The disorder influences only the two middle atoms of the propoxy groups and the occupation factors were refined to 0.50 (2):0.50 (2) for one propoxy group and 0.42 (2):0.58 (2) for the other (sites labelled *a* and *b* in Fig. 1). The large displacement parameters of the C atoms in the propoxy groups clearly indicate that additional disorder is present but this was not modelled since the data available did not warrant the introduction of more parameters.

Data collection: *MAD* (Allibon, 1995). Cell refinement: *MAD*. Data reduction: *KRYSTAL* (Hazell, 1995). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994) and *KRYSTAL*. Molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *KRYSTAL*. Software used to prepare material for publication: *KRYSTAL*.

We are indebted to the Carlsberg Foundation and to the Danish Science Research Council for financing the Huber diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1468). Services for accessing these data are described at the back of the journal.

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## A Benzannulated [5.3.1] Propellanone Related to the ABC Ring System of Taxol<sup>TM</sup>

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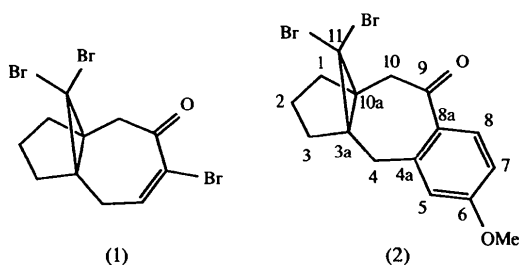
**Abstract**

The title compound, (3 $\alpha$ ,10 $\alpha$ )-11,11-dibromo-6-methoxy-2,3,3a,10a-tetrahydro-1*H*,4*H*-3a,10a-methanobenz[*f*]azulen-9(10*H*)-one, C<sub>16</sub>H<sub>16</sub>Br<sub>2</sub>O<sub>2</sub>, is shown to contain a C6-methoxylated aromatic ring and bears some resemblance to the ABC ring system of paclitaxel (Taxol<sup>TM</sup>).

**Comment**

In connection with efforts to use certain cyclohexannulated [5.3.1]propellanes for construction of the ABC ring system associated with the anticancer agent Taxol<sup>TM</sup> (Banwell, Gable, Peters & Phyland, 1995),

we had occasion to examine the Diels–Alder reaction of the [5.3.1]propellenone (1) with 1-methoxy-3-(trimethylsiloxy)-1,3-butadiene (Brownbridge, 1983). When a mixture of the diene and the dienophile was heated in refluxing benzene, a single adduct was obtained in high yield. However, this adduct proved to be unstable and, on standing, was converted into an aromatic product. Contrary to expectation, spectroscopic analysis of this product suggested the presence of a methoxylated rather than a hydroxylated aromatic ring. The unusual structure implied by this observation prompted a single-crystal X-ray analysis of the material. In this manner, structure (2) was established, which reveals that the molecule possesses a C<sub>6</sub>-methoxylated aromatic ring and bears some resemblance to the ABC ring system of Taxol™.



The molecular conformation is illustrated in Fig. 1 (Table 1). In the *cis*-fused cyclopentane ring, the 2 $\beta$ -envelope atoms C3, C3a, C10a and C1 are coplanar within experimental error, with C2 lying 0.1525 (8) Å out of the plane, and with pseudo-rotational parameters (Altona, Geize & Romers, 1968) of  $\Delta = 36.3^\circ$  and  $\varphi_m = 10.1^\circ$ . The cycloheptane ring adopts a regular boat conformation, with an asymmetry parameter (Duax & Norton, 1975)  $\Delta C_2^{3a,10a}$  of  $5.4^\circ$  and with atoms C4, C4a,

C8a and C9 coplanar to within 0.006 (3) Å, and atoms C4, C3a, C10a and C10 coplanar to within 0.005 (3) Å; the dihedral angle between the two planes is  $120.4 (2)^\circ$ .

## Experimental

Compound (2) was obtained by heating the [5.3.1]-propellenone (1) (Banwell & Phylard, 1994) with 3.5 molar equivalents of 1-methoxy-3-(trimethylsiloxy)-1,3-butadiene (Aldrich) in benzene at reflux for 6 h. The cooled reaction mixture was treated with mineral acid and the material obtained was subjected to chromatography on silica. In this manner, the title compound, (2), was obtained and recrystallized from an ethyl acetate–hexane mixture.

### Crystal data

C<sub>16</sub>H<sub>16</sub>Br<sub>2</sub>O<sub>2</sub>

$M_r = 400.2$

Triclinic

$P\bar{1}$

$a = 9.411 (1) \text{ \AA}$

$b = 10.427 (2) \text{ \AA}$

$c = 7.930 (2) \text{ \AA}$

$\alpha = 104.99 (1)^\circ$

$\beta = 103.74 (1)^\circ$

$\gamma = 92.72 (1)^\circ$

$V = 725.2 (2) \text{ \AA}^3$

$Z = 2$

$D_x = 1.832 \text{ Mg m}^{-3}$

$D_m$  not measured

Cu  $K\alpha$  radiation

$\lambda = 1.5418 \text{ \AA}$

Cell parameters from 25

reflections

$\theta = 18\text{--}32^\circ$

$\mu = 7.08 \text{ mm}^{-1}$

$T = 292 (2) \text{ K}$

Prismatic

$0.256 \times 0.256 \times 0.130 \text{ mm}$

Pale yellow

### Data collection

Rigaku AFC diffractometer

$\omega/2\theta$  scans

Absorption correction:

Gaussian (SHELX76;

Sheldrick, 1976)

$T_{\min} = 0.202$ ,  $T_{\max} = 0.465$

2422 measured reflections

2252 independent reflections

2089 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\text{max}} = 65.0^\circ$

$h = -11 \rightarrow 11$

$k = -12 \rightarrow 12$

$l = 0 \rightarrow 9$

3 standard reflections

every 100 reflections

intensity decay:  $< 2.5\%$

### Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.137$

$S = 1.081$

2252 reflections

185 parameters

Only H-atom  $U$ 's refined

$w = 1/[\sigma^2(F_o^2) + (0.1065P)^2 + 0.3562P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.030$

$\Delta\rho_{\text{max}} = 0.970 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.672 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0050 (8)

Scattering factors from

International Tables for Crystallography (Vol. C)

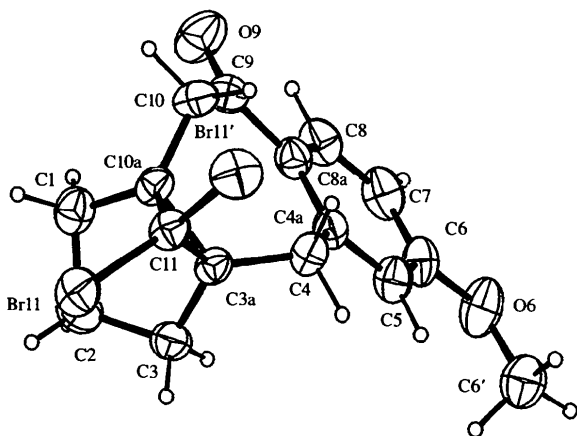


Fig. 1. Perspective view of the molecular structure of the 3aR,10aS enantiomer of (2). The displacement ellipsoids are drawn at the 50% probability level and the H atoms are denoted by spheres of arbitrary radii.

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

C1—C10a	1.516 (6)	C6—C7	1.399 (7)
C1—C2	1.547 (7)	O6—C6'	1.453 (6)
C2—C3	1.534 (7)	C7—C8	1.373 (7)

C3—C3a	1.515 (6)	C8—C8a	1.415 (6)
C3a—C11	1.507 (5)	C8a—C9	1.496 (6)
C3a—C4	1.520 (6)	C9—O9	1.222 (6)
C3a—C10a	1.526 (5)	C9—C10	1.506 (6)
C4—C4a	1.508 (6)	C10—C10a	1.514 (6)
C4a—C5	1.401 (6)	C10a—C11	1.510 (6)
C4a—C8a	1.412 (6)	C11—Br11'	1.929 (4)
C5—C6	1.392 (6)	C11—Br11	1.933 (4)
C6—O6	1.354 (5)		
C2—C1—C10a	106.9 (4)	C4a—C8a—C8	118.2 (4)
C1—C2—C3	107.9 (4)	C4a—C8a—C9	126.9 (4)
C2—C3—C3a	107.1 (4)	C8—C8a—C9	114.9 (4)
C3—C3a—C4	117.9 (4)	C8a—C9—O9	120.2 (4)
C3—C3a—C10a	108.7 (3)	C8a—C9—C10	121.3 (4)
C3—C3a—C11	117.4 (3)	O9—C9—C10	118.5 (4)
C4—C3a—C10a	117.8 (3)	C9—C10—C10a	111.3 (3)
C4—C3a—C11	120.7 (4)	C1—C10a—C3a	108.4 (3)
C10a—C3a—C11	59.7 (3)	C1—C10a—C10	118.4 (4)
C3a—C4—C4a	112.7 (3)	C1—C10a—C11	117.3 (4)
C4—C4a—C5	115.8 (4)	C3a—C10a—C10	118.4 (3)
C4—C4a—C8a	125.2 (4)	C3a—C10a—C11	59.5 (3)
C5—C4a—C8a	119.0 (4)	C10—C10a—C11	120.0 (4)
C4a—C5—C6	122.0 (4)	C3a—C11—C10a	60.8 (3)
C5—C6—O6	124.9 (4)	C3a—C11—Br11	120.9 (3)
C5—C6—C7	118.7 (4)	C3a—C11—Br11'	120.4 (3)
O6—C6—C7	116.4 (4)	C10a—C11—Br11	120.6 (3)
C6—O6—C6'	118.6 (4)	C10a—C11—Br11'	120.7 (3)
C6—C7—C8	120.3 (4)	Br11—C11—Br11'	107.5 (2)
C7—C8—C8a	121.8 (4)		
C1—C2—C3—C3a	9.6 (5)	C10—C10a—C3a—C4	-1.1 (6)
C2—C3—C3a—C10a	-6.0 (5)	C10a—C3a—C4—C4a	-66.6 (5)
C3—C3a—C10a—C1	0.1 (4)	C3—C3a—C11—Br11	13.6 (5)
C3a—C10a—C1—C2	5.9 (5)	C10—C10a—C11—Br11'	2.7 (5)
C10a—C1—C2—C3	-9.6 (5)	C4—C4a—C5—C6	-177.9 (4)
C3a—C4—C4a—C8a	53.0 (5)	C4a—C5—C6—O6	178.5 (4)
C4—C4a—C8a—C9	1.6 (6)	C5—C6—O6—C6'	-0.5 (7)
C4a—C8a—C9—C10	1.7 (6)	C10—C9—C8a—C8	-176.4 (4)
C8a—C9—C10—C10a	-59.0 (5)	C10a—C10—C9—O9	122.7 (5)
C9—C10—C10a—C3a	71.3 (5)		

Data collection: *AFCIMSC* (Rigaku Corporation, 1988). Cell refinement: *AFCIMSC*. Data reduction: *AFCIMSC*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1166). Services for accessing these data are described at the back of the journal.

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## 4,4'-Azinodimethyldipyridinium Dip perchlorate, $C_{12}H_{12}N_4^{2+} \cdot 2ClO_4^-$

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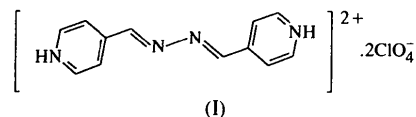
(Received 3 February 1997; accepted 18 April 1997)

## Abstract

The centrosymmetric 4,4'-azinodimethyldipyridinium cations,  $C_{12}H_{12}N_4^{2+}$ , are planar and lie in planes parallel to the *c* axis. There is a strong intermolecular hydrogen bond,  $N1—H \cdots O4^i$  [2.896 (3) Å; symmetry code: (i)  $-x, 1-y, -z$ ], and a number of weaker hydrogen bonds between the C atoms of the pyridine rings and the O atoms of the perchlorate anions [3.234–3.246 (4) Å].

## Comment

The cation of the title compound, (I), is well known as a precursor of atactic poly-4-vinylpyridine which has been used to coordinate transition metal ions such as  $Fe^{2+}$ ,  $Co^{2+}$  and  $Ni^{2+}$  (Biedermann, Obwandner & Wichmann, 1972). In addition, the Schiff base ligand derived from hydrazine has applications in coordination chemistry owing to its polydentate chelating ability (Tarafder & Khan, 1991). Although the synthesis and characterization of the 4,4'-azinodimethyldipyridinium cation have been discussed previously (Biedermann & Schmid, 1973; El-Rayyes & Katrib, 1983), its crystal structure, to the best of our knowledge, has not been reported; it is of interest to us owing to the cation's ability to act as a potential bridging ligand. In this paper, we report the crystal structure of 4,4'-azinodimethyldipyridinium dip perchlorate, (I).



An *ORTEPII* (Johnson, 1976) plot of the title compound is shown in Fig. 1. The  $N2=C6$  double-bond distance [1.260 (4) Å] is slightly shorter than that of another Schiff base compound derived from hydrazine, namely, 2,2'-azinodimethyldiphenol [ $C=N$  1.285 (7) Å; Xu, You & Sun, 1994], while the  $N2—N2^i$  single-bond distance [1.400 (4) Å; symmetry code: (i)  $-2-x,$