

atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Table 1 contains a list of atomic positional parameters while Table 2 gives interatomic distances and bond angles.\*

**Discussion.** Fig. 1 is a drawing of compound (4a). The molecule consists of a cage containing four five-membered rings in envelope conformations and a planar (0.005 Å r.m.s. deviation) four-membered ring. The cage is spiro fused to a *cis*-bicyclooctane ring and to an ethylenedioxy moiety. The bond lengths around the cage are statistically equivalent to the average values for compounds (5) (Flippin-Anderson, Gilardi, George, Marchand & Reddy, 1989) and (6) (Watson, Nagl, Marchand, Reddy & Reddy, 1989) except for the lengthening of C(1)—C(11) and C(10)—C(11) from an average of 1.515 (3) Å in (5) and (6) to 1.530 (5) Å in (4a) owing to the spiro fusion at C(11). The long bond at C(5)—C(6) of 1.568 (3) Å is consistent with the average value of 1.575 (2) Å observed in the reference compounds. C(4) is slightly pyramidalized, lying 0.075 (3) Å out of the plane of C(3)C(5)O(3).

\* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53030 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Molecular-mechanics calculations (*PCMODEL*, 1989) indicate the molecule has 267.3 kJ mol<sup>-1</sup> of strain energy distributed primarily between angle and torsional contributions.

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## Structure of a Bromonitro-Substituted 2-Oxapentacyclo[7.3.0.0<sup>3,7</sup>.0<sup>4,12</sup>.0<sup>6,10</sup>]dodecane

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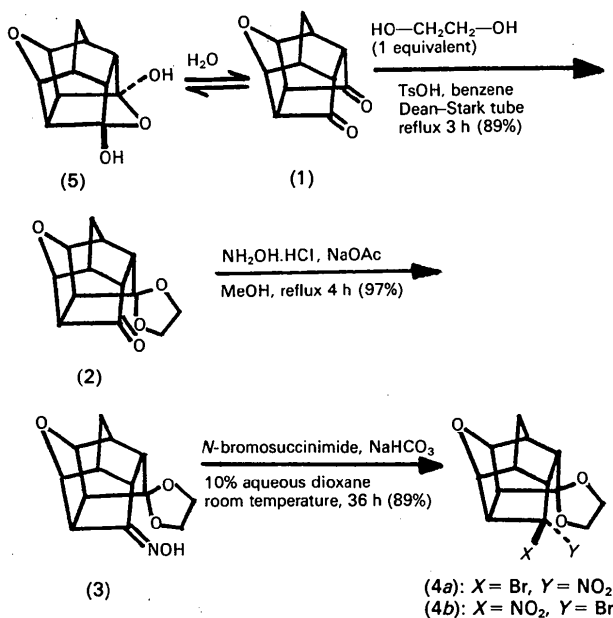
**Abstract.** 5-Bromo-11-ethylenedioxy-5-nitro-2-oxapentacyclo[7.3.0.0<sup>3,7</sup>.0<sup>4,12</sup>.0<sup>6,10</sup>]dodecane, (4a), C<sub>13</sub>H<sub>14</sub>BrNO<sub>5</sub>, *M<sub>r</sub>* = 344.17, monoclinic, *P*2<sub>1</sub>/*a*, *a* = 9.296 (1), *b* = 10.664 (2), *c* = 12.508 (1) Å, β = 93.41°, *V* = 1237.7 (2) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.847 g cm<sup>-3</sup>, λ(Mo Kα) = 0.71073 Å, μ = 33.0 cm<sup>-1</sup>, *F*(000) = 696, *T* = 295 K, *R* = 0.0470 for 2270 reflections. The

compound is an open-ended cage containing four five-membered rings in envelope conformations and a six-membered heterocyclic ring in a boat conformation. Steric crowding may have a greater effect upon bond lengths than the bromonitro substitution at C(8).

**Introduction.** As part of a program that is concerned with the synthesis and chemistry of novel, substi-

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tuted pentacyclo[5.4.0.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>]undecanes (Marchand, 1989), we recently reported the synthesis and structure of a heteropolycyclic cage diketone, (1) (Marchand, Reddy, Watson, & Kashyap, 1990). This compound could be converted to the corresponding mono(ethylene ketal), (2), in 89% yield *via* reaction with one equivalent of ethylene glycol in the presence of a catalytic amount of *p*-toluenesulfonic acid. Compound (2) was converted to the corresponding oxime, (3) *via* reaction with hydroxylamine hydrochloride in the presence of sodium acetate (Corey, Melvin, & Haslanger, 1975; Marchand, Arney & Dave, 1988). Subsequently, (3) was converted into the corresponding geminal bromonitro compound by following a previously published procedure (Marchand, Dave, Rajapaksa & Arney, 1989). Although conceivably two products might have been formed *via* oxidative bromination of (3) [*i.e.* (4*a*) and (4*b*)], only one product, in fact, was obtained from this reaction (89% yield). The structure of that product was established as being (4*a*) [rather than (4*b*)] by single-crystal X-ray structural analysis.



**Experimental.** A colorless single crystal of dimensions 0.38 × 0.38 × 0.25 mm was mounted on a Nicolet R3m/μ update of a P2<sub>1</sub> diffractometer; data collected in the ω-scan mode (3 ≤ 2θ ≤ 55°), using a variable scan rate (4 to 29.3° min<sup>-1</sup>) and graphite-monochromated Mo Kα radiation; lattice parameters from a least-squares refinement of 25 reflections (24.35 ≤ 2θ ≤ 28.58°); systematic absences (h0l, h = 2n + 1; 0k0, h = 2n + 1) consistent with space group P2<sub>1</sub>/a; reference reflections (2̄52) and 03̄5) showed less than a 2% random variation in intensities (linear correction); 3170 reflections measured (-12 ≤ h ≤

Table 1. Atomic coordinates (× 10<sup>4</sup>) and equivalent isotropic thermal parameters (Å<sup>2</sup> × 10<sup>3</sup>)

$U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U_{\text{eq}}$
C(1)	2830 (4)	-1585 (3)	7627 (3)	27 (1)
C(2)	4425 (4)	-1743 (3)	7429 (3)	29 (1)
C(3)	5177 (3)	-529 (3)	7900 (2)	29 (1)
C(4)	5714 (4)	233 (4)	6992 (3)	38 (1)
C(5)	4300 (4)	523 (3)	6391 (3)	32 (1)
C(6)	3605 (4)	-728 (3)	5975 (2)	32 (1)
C(7)	2225 (4)	-885 (3)	6601 (2)	25 (1)
C(8)	1866 (3)	469 (3)	6816 (2)	23 (1)
C(9)	3303 (4)	962 (3)	7270 (3)	25 (1)
C(10)	3911 (4)	245 (3)	8296 (2)	27 (1)
C(11)	2924 (4)	-783 (3)	8638 (2)	30 (1)
O(1)	4486 (3)	-1776 (2)	6286 (2)	37 (1)
O(2)	3661 (3)	-1477 (2)	9486 (2)	41 (1)
C(12)	2602 (4)	-1947 (4)	10125 (3)	53 (2)
C(13)	1350 (4)	-1116 (4)	9932 (3)	54 (2)
O(3)	1623 (3)	-387 (2)	9048 (2)	45 (1)
Br	1311 (1)	1349 (1)	5464 (1)	38 (1)
N	522 (3)	721 (3)	7413 (2)	30 (1)
O(4)	484 (3)	1699 (2)	7907 (2)	39 (1)
O(5)	-439 (3)	-51 (2)	7325 (2)	46 (1)

12; 0 ≤ k ≤ 13; 0 ≤ l ≤ 16), 2830 independent ( $R_{\text{merge}} = 0.0094$ ), 2270 with  $I \geq 3\sigma(I)$ ; Lorentz-polarization corrections and a ψ-scan-based empirical absorption correction applied (transmission factors 0.208 to 0.268); structure solved by direct methods and refined by a block-cascade least-squares procedure, H atoms located in difference map, four H atoms of the ethylene ketal allowed to ride on attached C atom with refined isotropic thermal parameters positional parameters and isotropic thermal parameters refined for remaining H atoms; final  $R = 0.0470$  ( $R_{\text{all}} = 0.0625$ ),  $wR = 0.0253$  ( $wR_{\text{all}} = 0.0259$ ) for 226 parameters and 2270 reflections,  $S = 1.751$ ,  $(\Delta/\sigma)_{\text{max}} = 0.014$ , largest peaks in final difference map of -0.56 and 0.49 e Å<sup>-3</sup>;  $\sum w(|F_o| - |F_c|)^2$  refined with  $w = 1/\sigma^2(F_o)$ ; isotropic extinction corrections applied,  $F = F_c/[1.0 + 1.2(3) \times 10^6 F_c^2/\sin(2\theta)]^{0.25}$ . All computer programs for Desktop 30 (Microclipse) and Nova 4/C configuration supplied by Nicolet (Nicolet Instrument Corporation, 1986); atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic positional parameters are listed in Table 1 while selected bond lengths and angles are given in Table 2.\*

**Discussion.** Fig. 1 is a drawing of compound (4*a*). The compound is an open-ended cage structure containing four five-membered rings in envelope confor-

\* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53119 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°) for compound (4a)

C(1)—C(2)	1.527 (5)	C(1)—C(7)	1.560 (4)
C(1)—C(11)	1.526 (4)	C(2)—C(3)	1.570 (5)
C(2)—O(1)	1.435 (4)	C(3)—C(4)	1.505 (5)
C(3)—C(10)	1.543 (5)	C(4)—C(5)	1.507 (5)
C(5)—C(6)	1.558 (5)	C(5)—C(9)	1.551 (5)
C(6)—C(7)	1.551 (5)	C(6)—O(1)	1.426 (4)
C(7)—C(8)	1.510 (4)	C(8)—C(9)	1.514 (4)
C(8)—Br	1.976 (3)	C(8)—N	1.518 (4)
C(9)—C(10)	1.570 (4)	C(10)—C(11)	1.507 (5)
C(11)—O(2)	1.434 (4)	C(11)—O(3)	1.406 (4)
O(2)—C(12)	1.397 (5)	C(12)—C(13)	1.471 (6)
C(13)—O(3)	1.387 (5)	N—O(4)	1.213 (3)
N—O(5)	1.215 (4)		
C(2)—C(1)—C(7)	103.1 (3)	C(2)—C(1)—C(11)	100.8 (3)
C(7)—C(1)—C(11)	114.4 (3)	C(1)—C(2)—C(3)	105.3 (3)
C(1)—C(2)—O(1)	105.1 (3)	C(3)—C(2)—O(1)	110.5 (3)
C(2)—C(3)—C(4)	108.8 (3)	C(2)—C(3)—C(10)	103.3 (3)
C(4)—C(3)—C(10)	104.3 (3)	C(3)—C(4)—C(5)	99.7 (3)
C(4)—C(5)—C(6)	108.9 (3)	C(4)—C(5)—C(9)	104.4 (3)
C(6)—C(5)—C(9)	104.0 (3)	C(5)—C(6)—C(7)	105.2 (3)
C(5)—C(6)—O(1)	111.1 (3)	C(7)—C(6)—O(1)	104.9 (3)
C(1)—C(7)—C(6)	101.4 (3)	C(1)—C(7)—C(8)	112.6 (2)
C(6)—C(7)—C(8)	100.6 (3)	C(7)—C(8)—C(9)	101.5 (2)
C(7)—C(8)—Br	110.6 (2)	C(9)—C(8)—Br	109.6 (2)
C(7)—C(8)—N	117.0 (3)	C(9)—C(8)—N	119.2 (2)
Br—C(8)—N	99.0 (2)	C(5)—C(9)—C(8)	100.4 (2)
C(5)—C(9)—C(10)	103.3 (3)	C(8)—C(9)—C(10)	113.8 (3)
C(3)—C(10)—C(9)	104.0 (2)	C(3)—C(10)—C(11)	101.0 (3)
C(9)—C(10)—C(11)	113.0 (3)	C(1)—C(11)—C(10)	100.3 (2)
C(1)—C(11)—O(2)	109.0 (3)	C(10)—C(11)—O(2)	108.3 (2)
C(1)—C(11)—O(3)	117.5 (3)	C(10)—C(11)—O(3)	115.9 (3)
O(2)—C(11)—O(3)	105.6 (2)	C(2)—O(1)—C(6)	101.3 (2)
C(11)—O(2)—C(12)	106.7 (3)	O(2)—C(12)—C(13)	105.5 (3)
C(12)—C(13)—O(3)	106.7 (3)	C(11)—O(3)—C(13)	108.9 (3)
C(8)—N—O(4)	116.9 (2)	C(8)—N—O(5)	117.2 (3)
O(4)—N—O(5)	125.8 (3)		

mations and a six-membered ring in a boat conformation. In the related compound (5) (Marchand, Reddy, Watson & Kashyap, 1990) the open end of the cage is closed with an oxa group forming a symmetric molecule with two additional five-membered rings in envelope conformations. A non-crystallographic mirror plane bisects the molecule with mirror-related bonds statistically equivalent in length. In compound (4a) the substituents at C(8) and C(11) are electronically and sterically different, and it is difficult to predict *a priori* their effects on the bond lengths and angles. This is particularly true of the bromonitro substitution at C(8). Some of the bonds related by a pseudo mirror plane through O(1), C(4) and the midpoint of C(1)—C(7) are statistically different in length. One might expect the greatest variations to involve C atoms C(8) and C(11); however, the C(8)—C(9) and C(10)—C(11) distances of 1.514 (4) and 1.507 (5) Å are equivalent while C(1)—C(11) = 1.526 (4) and C(7)—C(8) = 1.510 (4) Å differ by slightly more than 3 $\sigma$ . The major discrepancy is between C(1)—C(2) = 1.527 (5) and C(6)—C(7) = 1.551 (5) Å which is more difficult to rationalize. There are three sets of bonds in (4a)

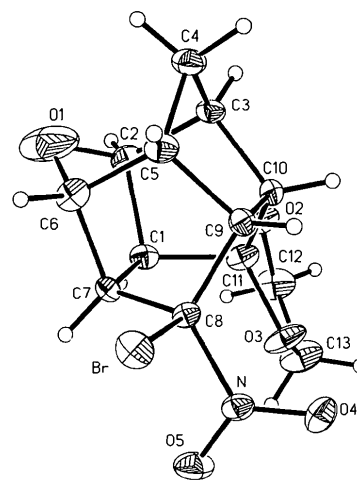


Fig. 1. Drawing of compound (4a) with thermal ellipsoids at the 35% probability level. H atoms are represented by spheres of arbitrary size.

which are longer than 1.56 Å. The C(2)—C(3) and C(5)—C(6) bond average of 1.564 (6) Å compares well with the value of 1.561 (1) Å found in (5). The C(9)—C(10) distance in the parent diketone and molecules with  $\pi$  electrons at C(8) and C(11) averages 1.590 (5) Å which is attributed to a through-bond coupling of the  $\pi$  electrons (Watson, Nagl, Marchand, Reddy & Reddy, 1989; Osawa & Kanematsu, 1986). In compounds such as (5) this  $\pi$  coupling does not exist and the bond is shortened to 1.556 (2) Å; however, in (4a) the distance is 1.570 (5) Å which may suggest steric crowding at C(8) and C(11) where N...O(3) = 2.525 (4) Å. The C(1)—C(7) distance in (4a) is 1.560 (5) Å as compared with 1.549 (2) Å in (5). Molecular-mechanics calculations (PCMODEL, 1989) estimate the strain energy in (4a) to be 218.1 kJ mol<sup>-1</sup> and that in (5) to be 147.8 kJ mol<sup>-1</sup> with the primary contributor a difference in van der Waals interactions, 68.7 and 16.7 kJ mol<sup>-1</sup> in (4a) and (5), respectively.

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## Structure of (1*S*,3*R*,4*R*,8*S*,9*R*)-1-*tert*-Butyldiphenylsilyloxy-4-hydroxymethyl-2,5,7-trioxa-12-azatricyclo[7.3.1.0<sup>3,8</sup>]tridecan-11-one, an Intermediate in the Synthesis of (+)-Sesbanimide A

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**Abstract.** C<sub>26</sub>H<sub>33</sub>NO<sub>6</sub>Si, *M*<sub>r</sub> = 483.6, monoclinic, *P*2<sub>1</sub>, *a* = 15.186 (3), *b* = 27.498 (4), *c* = 14.437 (2) Å, β = 115.66 (1)°, *V* = 5434 (2) Å<sup>3</sup>, *Z* = 8, *D*<sub>x</sub> = 1.18 g cm<sup>-3</sup>, λ(Cu Kα) = 1.5418 Å, μ = 10.6 cm<sup>-1</sup>, *F*(000) = 2064, room temperature, final *R* = 0.084 for 4774 observed reflections. The asymmetric unit contains four independent molecules. One of the four molecules shows a relative positioning of the substituents of the Si atom that differs from the other three. Two pairs of molecules are identically linked by hydrogen bridges.

**Introduction.** The compound (+)-sesbanimide A, which can be extracted from the seeds of *Sesbania drummondii*, is an active anti-leukemic alkaloid. The structure presented here is that of an intermediate in the synthesis of (+)-sesbanimide A as described by Vloon, van den Bos, Willard, Koomen & Pandit (1989); the X-ray crystallographic study confirms the proposed tricyclic nature of the title compound.

**Experimental.** A brick-shaped crystal (approximate dimensions 0.13 × 0.23 × 0.30 mm) was used for data collection on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Cu Kα radiation and θ–2θ scan. A total of 5720 unique reflections were measured within the range –15 ≤ *h* ≤ 13, 0 ≤ *k* ≤ 27, 0 ≤ *l* ≤ 14. Of these, 4774 were above the significance level of 2.5σ(*I*). The maximum value of (sinθ)/λ was 0.50 Å<sup>-1</sup>. Two standard reflections (130,  $\bar{1}$ 11) were measured hourly, no significant

decrease in intensity was measured during the 66 h collecting time. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with 66 < 2θ < 70°. Corrections for Lorentz and polarization effects were applied. The structure was solved by direct methods using the XTAL system of crystallographic programs (Hall & Stewart, 1987). Structure factors were normalized using a profile scale and some 10 000 triplets and 6000 quartets for the strongest 999 reflections were included in a tangent phase extension and refinement using a magic cascade procedure. The Fourier map revealed some eighty atoms, mainly showing parts of the tricyclic systems. A subsequent iterative procedure, consisting of a least-squares refinement of the current model, an *F*<sub>obs</sub> Fourier synthesis and a manual interpretation of the resulting peaks, completed the model.

The positions of the H atoms were calculated. Anisotropic block-diagonal least-squares refinement on *F*, keeping the H atoms fixed at their calculated positions with *U* = 0.06 Å<sup>2</sup>, converged to *R* = 0.084, *wR* = 0.126, (Δ/σ)<sub>max</sub> = 0.21, origin defined by fixing *y* of C(1A). A weighting scheme *w* = (6.2 + *F*<sub>obs</sub> + 0.01*F*<sub>obs</sub><sup>2</sup>)<sup>-1</sup> was used. An empirical absorption correction was applied, with corrections in the range 0.53–1.22 (Walker & Stuart, 1983). The isotropic secondary-extinction coefficient refined to 2.6 (1) × 10<sup>-2</sup> (Zachariasen, 1968). A final difference Fourier map revealed a residual electron density between –0.3 and 1.2 e Å<sup>-3</sup>. Scattering factors were taken from Cromer & Mann (1968). Anomalous-dispersion