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Structures of Two Derivatives of 1,2,4-Trioxane

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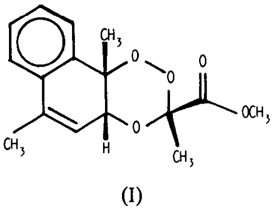
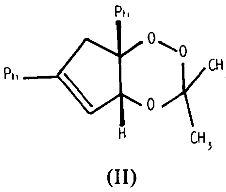
Abstract. (I): *cis*-4a,10b-Dihydro-3,6,10b-trimethylnaphtho[2,1-*e*][1,2,4]trioxin-3-carboxylic acid methyl ester, $C_{16}H_{18}O_5$, $M_r = 290\cdot3$, monoclinic, $P2_1/a$, $a = 24\cdot474\ (4)$, $b = 7\cdot798\ (8)$, $c = 8\cdot150\ (8)$ Å, $\beta = 106\cdot95\ (2)°$, $U = 1487\cdot8\ (3)$ Å^3, $Z = 4$, $D_x = 1\cdot30$ Mg m^{-3}, $\lambda(\text{Cu}\ K\alpha) = 1\cdot54178$ Å, $\mu = 0\cdot710$ mm^{-1}, $F(000) = 616$, $T = 293$ K, final $R = 0\cdot047$ for 2367 unique diffractometer data $[F_o > 3\sigma(F_o)]$. (II): *cis*-4a,7a-Dihydro-3,3-dimethyl-6,7a-diphenyl-7*H*-cyclopenta[1,2,4]trioxin, $C_{20}H_{20}O_3$, $M_r = 308\cdot4$, monoclinic, $P2_1/c$, $a = 17\cdot144\ (4)$, $b = 5\cdot771\ (1)$, $c = 17\cdot720\ (4)$ Å, $\beta = 110\cdot64\ (2)°$, $U = 1640\cdot7\ (6)$ Å^3, $Z = 4$, $D_x = 1\cdot25$ Mg m^{-3}, $\lambda(\text{Cu}\ K\alpha) = 1\cdot54178$ Å, $\mu = 0\cdot584$ mm^{-1}, $F(000) = 656$, $T = 293$ K, final $R = 0\cdot042$ for 2577 unique diffractometer data $[F_o > 3\sigma(F_o)]$. *cis*-Fusion of 1,2,4-trioxane [to cyclohexadiene in (I) and cyclopentene in (II)] is confirmed. The heterocycle adopts a chair conformation in (I) and a twist-boat form in (II). The C—O bond lengths in (I) and (II) cover a wide range [1·401 (1)–1·444 (1) Å], as is found in other trioxanes.

Introduction. The 1,2,4-trioxane ring is the key substructural feature of the antimalarial *Qinghaosu* [Qinghaosu Antimalarial Coordinating Research Group, 1979; crystal structure: Academica Sinica Qingahaosu Research Group (hereinafter ASQRG), 1980]. There is considerable current pharmaceutical and structural interest in this unusual heterocycle, for which few reliable synthetic routes were previously known. Recently, however, Jefford and co-workers have shown that high yields of 1,2,4-trioxanes are produced *via* catalytic reactions of ketones and aldehydes with 1,2-dioxetanes (Jefford, Boukouvalas & Kohmoto, 1983), 1,4-endoperoxides (Jefford, Jaggi, Boukouvalas & Kohmoto, 1983), and allylic hydroperoxides (Jefford, Jaggi, Kohmoto, Boukouvalas & Bernardinelli, 1984). Here we present X-ray results for two derivatives (I, II) prepared *via* the second of these synthetic routes.



(I)



(II)

Experimental. (I): Colourless needles, crystal 0·15 × 0·20 × 0·43 mm, Nicolet $P2_1$ diffractometer, unit-cell parameters derived from 15 reflections with $36 < 2\theta < 85°$, $\omega/2\theta$ scan mode with variable scan rate (3–29·3° min^{-1}), 3355 reflections measured in two

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overlapping shells (i) 3–90°, (ii) 85–130°, three standard reflections measured after every 50 reflections showed no significant variation. Data reduction employed profile analysis, absorption correction not applied, 2541 unique reflections ($R_{\text{int}} = 0{\cdot}006$) where 172 with $F < 3\sigma(F)$ were classified as unobserved. (II): colourless rhombs, crystal $0{\cdot}25 \times 0{\cdot}31 \times 0{\cdot}23$ mm, Nicolet $P2_1$ diffractometer, unit-cell parameters derived from 15 reflections with $50 < 2\theta < 65°$, 3479 reflection intensities recorded and processed as for (I), 2742 unique reflections ($R_{\text{int}} = 0{\cdot}009$) where 165 with $F < 3\sigma(F)$ were classified as unobserved.

(I) and (II): structure solution by automated direct methods, all H atoms located from difference syntheses, full-matrix refinement with C, O anisotropic, H-atom positions refined, together with three isotropic *U* values for (i) benzenoid H, (ii) methyl H, (iii) ring-framework H, scattering factors from *International Tables for X-ray Crystallography* (1974), all calculations performed with *SHELX*76 (Sheldrick, 1976). For (I): $w^{-1} = \sigma^2(F) + 0{\cdot}0005F^2$, 247 parameters, 2 reflections omitted for extinction, $R = 0{\cdot}047$, $wR = 0{\cdot}057$, maximum shift/e.s.d. = 0·20, mean = 0·04, maximum peak in final difference map = 0·21 e Å^{-3}, largest trough = 0·18 e Å^{-3}. For (II): $w^{-1} = \sigma^2(F)$, 271 parameters, $R = 0{\cdot}042$, $wR = 0{\cdot}046$, maximum shift/e.s.d. = 0·41, mean = 0·08, maximum peak in final difference map = 0·16 e Å^{-3}, largest trough = 0·10 e Å^{-3}.

Table 1. *Atomic coordinates* ($\times 10^5$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^4$) *for* (I) *and* (II)

$U_{\text{eq}} = \frac{1}{3}$(trace of the orthogonalized U_{ij} matrix).

	x	*y*	*z*	U_{eq}
Compound (I)				
O(1)	36320 (3)	13135 (13)	64349 (11)	497 (4)
O(2)	30664 (3)	17799 (13)	65714 (13)	489 (4)
C(3)	30500 (6)	35895 (18)	66018 (19)	469 (5)
O(4)	34443 (3)	42098 (13)	80958 (13)	493 (4)
C(5)	40230 (6)	36258 (19)	83713 (19)	479 (5)
C(6)	43391 (6)	40922 (22)	101737 (20)	548 (6)
C(7)	43784 (6)	30322 (22)	114869 (19)	543 (5)
C(8)	41215 (6)	13100 (19)	111833 (19)	488 (5)
C(9)	39371 (6)	6506 (18)	95051 (18)	457 (5)
C(10)	40419 (6)	16966 (19)	80656 (18)	461 (5)
C(11)	37086 (6)	−9751 (20)	92140 (23)	559 (6)
C(12)	36524 (7)	−19788 (25)	105591 (26)	657 (7)
C(13)	38245 (7)	−13489 (25)	122066 (25)	667 (7)
C(14)	40566 (7)	2673 (26)	125142 (20)	624 (6)
C(15)	46066 (7)	11886 (26)	77758 (23)	597 (6)
C(16)	24615 (7)	40578 (25)	66729 (23)	586 (6)
C(17)	31656 (6)	43216 (19)	49682 (19)	526 (6)
O(18)	28587 (5)	34924 (15)	35971 (14)	619 (4)
C(19)	29025 (11)	40900 (35)	19620 (25)	761 (9)
O(20)	34709 (6)	55125 (18)	49637 (16)	756 (5)
C(21)	46719 (10)	35966 (35)	132861 (26)	787 (9)
Compound (II)				
O(1)	16973 (6)	4741 (16)	11690 (6)	574 (4)
O(2)	8265 (6)	11777 (19)	7577 (6)	595 (4)
C(3)	5490 (9)	21210 (28)	13717 (9)	555 (6)
O(4)	11988 (6)	35127 (18)	19053 (5)	533 (4)
C(5)	17445 (9)	45282 (25)	15424 (7)	479 (5)
C(6)	24637 (9)	55593 (25)	22004 (9)	508 (5)
C(7)	31589 (9)	43177 (25)	23778 (7)	513 (5)
C(8)	30251 (10)	22096 (28)	18410 (9)	555 (6)
C(9)	21552 (9)	25710 (23)	11975 (7)	477 (5)
C(10)	3680 (13)	2278 (35)	18735 (11)	707 (8)
C(11)	−2072 (10)	35439 (38)	8996 (11)	700 (7)
C(12)	22056 (7)	31326 (23)	3776 (7)	479 (5)
C(13)	25392 (10)	52235 (29)	2498 (10)	612 (7)
C(14)	26352 (13)	56831 (34)	−4786 (10)	743 (8)
C(15)	23866 (11)	40918 (35)	−10935 (10)	708 (7)
C(16)	20386 (11)	20473 (34)	−9851 (10)	714 (7)
C(17)	19507 (10)	15590 (29)	−2504 (9)	616 (7)
C(18)	39767 (9)	47865 (28)	30128 (9)	570 (6)
C(19)	41232 (11)	67864 (37)	34806 (10)	737 (7)
C(20)	48817 (14)	71865 (46)	40849 (11)	874 (9)
C(21)	55159 (14)	55988 (49)	42369 (13)	898 (10)
C(22)	53886 (13)	36422 (50)	37787 (15)	981 (11)
C(23)	46293 (11)	32402 (38)	31665 (13)	798 (8)

Discussion. The final fractional coordinates for (I) and (II) are given in Table 1.[*] Bond lengths and valence angles are given in Table 2. The molecular structures, depicted in Figs. 1 and 2 (*PLUTO*: Motherwell, 1978), confirm the *cis* fusion of the 1,2,4-trioxane ring to cyclohexadiene in (I) and cyclopentene in (II). The ester group in (I) is axial as suggested by NMR results (Jefford, 1983). Intra-annular torsion angles for the non-aromatic rings of (I) and (II) are compared in Table 3. In (I) the trioxane adopts a chair conformation with a mean torsion angle ($\bar{\omega}$) of 58·3°, whilst the cyclohexadiene is a flattened half-chair. In (II) the trioxane assumes the twist-boat conformation with maximal puckering about O(1)—O(2); the cyclopentene is an envelope with C(6) as flap.

The structures of (I) and (II) now bring the total number of 1,2,4-trioxane derivatives in the crystallographic literature to eight. Cambridge Structural Database (CSD) reference codes (Allen *et al.*, 1979) and short-form references are in Table 4(*a*), together with details of conformation and fusion geometry. Six of the rings adopt the chair conformation: three are *cis*-fused, one is *trans*-fused and there are two free rings. Mean torsion angles for all six examples are in Table 3. The O(1)—O(2) torsion angle is consistently high, with a mean of 69·1 (7)° for a range of 67·3–71·5°. By contrast, the torsion angles O(4)—C(5) and C(5)—C(10) average to 51·3 (12)° for twelve values in the range 42·9–57·7°. This increased puckering at O(1),O(2) is typical of chair-form cyclohexyl endoperoxides: in 1,2-dioxanes the O(1),O(2) torsion angle averages to 72·4 (2)° (range 71·2–74·0°) for 11 independent unfused rings contained in the four structures identified in Table 4(*b*). It is well known that *ROOR* torsion angles in simple peroxides are predominately in the range 90–120° (see, for example, Glidewell, Liles, Walton & Sheldrick, 1979), corresponding to one of the minima in the twofold O—O torsional potential (Hunt, Leacock, Peters & Hecht, 1965). Hence the increased peroxy puckering in cyclohexyl endoperoxides has been ascribed (Ridell, 1980) to a reduction in O—O torsional strain with increasing angle.

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[*] Lists of structure factors, anisotropic thermal parameters and atomic coordinates, bond lengths and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42787 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

However, the barrier to rotation about the O—O bond is small, being 4·62 kJ mol^{-1} towards the *trans* conformation and 29·4 kJ mol^{-1} towards the *cis* (Hunt, Leacock, Peters & Hecht, 1965), and certainly not more than ~12 kJ mol^{-1} in the torsional-angle range 60–270°. Hence torsional-energy factors may not be the sole reason for peroxy puckering: it should be noted that such puckering also results in a decrease in C—O—O valence angles, which would otherwise be unfavourably large. The mean C—O—O angle in the six chair-form trioxanes of Table 4(*a*) is 107·2 (5)°, whilst the corresponding value for the 1,2-dioxanes of Table 4(*b*) is identical [107·2 (3)°]. Conformations of cyclohexyl endoperoxides are currently being examined by molecular-mechanics calculations in this laboratory.

Table 2. *Bond lengths* (Å) *and valence angles* (°) *for the* C *and* O *atoms of compounds* (I) *and* (II)

Compound (I)

O(1)–C(10)	1·444 (2)	C(11)–C(12)	1·386 (3)
O(1)–O(2)	1·467 (1)	C(12)–C(13)	1·375 (3)
O(2)–C(3)	1·412 (2)	C(13)–C(14)	1·375 (3)
C(3)–O(4)	1·401 (2)	C(8)–C(14)	1·401 (2)
O(4)–C(5)	1·442 (2)	C(7)–C(21)	1·498 (2)
C(5)–C(10)	1·528 (2)	C(10)–C(15)	1·521 (2)
C(5)–C(6)	1·492 (2)	C(3)–C(16)	1·503 (2)
C(6)–C(7)	1·333 (2)	C(3)–C(17)	1·549 (2)
C(7)–C(8)	1·473 (2)	C(17)–O(18)	1·320 (2)
C(8)–C(9)	1·407 (2)	O(18)–C(19)	1·445 (2)
C(9)–C(10)	1·511 (2)	C(17)–O(20)	1·192 (2)
C(9)–C(11)	1·378 (2)		

C(10)–O(1)–O(2)	107·3 (1)	C(7)–C(8)–C(9)	119·8 (1)
C(3)–O(2)–O(1)	106·3 (1)	C(11)–C(9)–C(8)	120·2 (1)
O(2)–C(3)–O(4)	110·1 (1)	C(10)–C(9)–C(8)	118·6 (1)
C(17)–C(3)–O(4)	111·6 (1)	C(10)–C(9)–C(11)	121·0 (1)
C(17)–C(3)–O(2)	109·9 (1)	C(9)–C(10)–O(1)	111·9 (1)
C(16)–C(3)–O(4)	107·9 (1)	C(5)–C(10)–O(1)	107·9 (1)
C(16)–C(3)–O(2)	106·0 (1)	C(5)–C(10)–C(9)	112·6 (1)
C(16)–C(3)–C(17)	111·2 (1)	C(15)–C(10)–O(1)	102·8 (1)
C(3)–O(4)–C(5)	115·0 (1)	C(15)–C(10)–C(9)	110·3 (1)
C(10)–C(5)–O(4)	111·1 (1)	C(15)–C(10)–C(5)	110·7 (1)
C(6)–C(5)–O(4)	106·3 (1)	C(9)–C(11)–C(12)	120·8 (2)
C(6)–C(5)–C(10)	111·6 (1)	C(11)–C(12)–C(13)	119·8 (2)
C(7)–C(6)–C(5)	122·3 (1)	C(12)–C(13)–C(14)	119·9 (2)
C(6)–C(7)–C(8)	120·2 (1)	C(13)–C(14)–C(8)	121·7 (2)
C(21)–C(7)–C(8)	119·4 (2)	O(18)–C(17)–O(20)	125·6 (2)
C(21)–C(7)–C(6)	120·3 (2)	C(3)–C(17)–O(20)	124·2 (1)
C(9)–C(8)–C(14)	117·6 (1)	C(3)–C(17)–O(18)	110·2 (1)
C(7)–C(8)–C(14)	122·6 (1)	C(19)–O(18)–C(17)	116·5 (2)

Compound (II)

O(1)–C(9)	1·433 (2)	C(12)–C(13)	1·388 (2)
O(1)–O(2)	1·469 (2)	C(13)–C(14)	1·383 (2)
O(2)–C(3)	1·439 (2)	C(14)–C(15)	1·373 (3)
C(3)–O(4)	1·428 (2)	C(15)–C(16)	1·366 (3)
O(4)–C(5)	1·434 (2)	C(16)–C(17)	1·391 (2)
C(5)–C(6)	1·490 (2)	C(12)–C(17)	1·383 (2)
C(5)–C(9)	1·564 (2)	C(7)–C(18)	1·481 (2)
C(6)–C(7)	1·330 (2)	C(18)–C(19)	1·391 (2)
C(7)–C(8)	1·511 (2)	C(19)–C(20)	1·382 (3)
C(8)–C(9)	1·539 (2)	C(20)–C(21)	1·374 (3)
C(3)–C(10)	1·509 (2)	C(21)–C(22)	1·363 (4)
C(3)–C(11)	1·513 (2)	C(22)–C(23)	1·389 (3)
C(9)–C(12)	1·521 (2)	C(18)–C(23)	1·381 (3)

C(9)–O(1)–O(2)	103·4 (1)	C(12)–C(9)–O(1)	111·2 (1)
C(3)–O(2)–O(1)	106·2 (1)	C(12)–C(9)–C(5)	113·8 (1)
O(4)–C(3)–O(2)	108·9 (1)	C(12)–C(9)–C(8)	111·7 (1)
C(10)–C(3)–O(2)	111·3 (1)	C(13)–C(12)–C(9)	120·5 (1)
C(10)–C(3)–O(4)	107·0 (1)	C(17)–C(12)–C(9)	121·4 (1)
C(11)–C(3)–O(2)	103·6 (1)	C(17)–C(12)–C(13)	118·1 (1)
C(11)–C(3)–O(4)	112·2 (1)	C(14)–C(13)–C(12)	120·7 (2)
C(11)–C(3)–C(10)	113·9 (1)	C(15)–C(14)–C(13)	120·4 (2)
C(5)–O(4)–C(3)	114·4 (1)	C(16)–C(15)–C(14)	119·7 (2)
C(9)–C(5)–O(4)	109·5 (1)	C(17)–C(16)–C(15)	120·2 (2)
C(6)–C(5)–O(4)	107·6 (1)	C(16)–C(17)–C(12)	120·8 (2)
C(6)–C(5)–C(9)	103·4 (1)	C(19)–C(18)–C(7)	121·9 (2)
C(7)–C(6)–C(5)	113·3 (1)	C(23)–C(18)–C(7)	121·1 (2)
C(6)–C(7)–C(8)	111·1 (1)	C(23)–C(18)–C(19)	117·1 (2)
C(18)–C(7)–C(8)	121·2 (1)	C(20)–C(19)–C(18)	121·6 (2)
C(18)–C(7)–C(6)	127·6 (1)	C(21)–C(20)–C(19)	120·3 (2)
C(7)–C(8)–C(9)	104·4 (1)	C(22) C(21)–C(20)	119·1 (2)
C(5)–C(9)–O(1)	107·9 (1)	C(23)–C(22)–C(21)	120·9 (2)
C(8)–C(9)–O(1)	106·7 (1)	C(22)–C(23)–C(18)	121·1 (2)
C(8)–C(9)–C(5)	105·1 (1)		

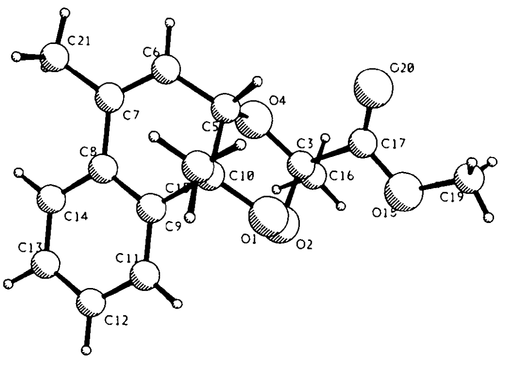

Fig. 1. Perspective view of the molecular structure of (I).

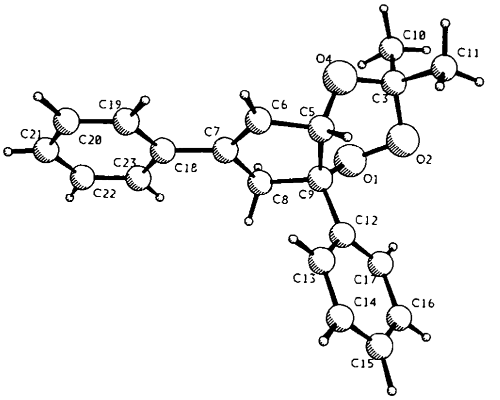

Fig. 2. Perspective view of the molecular structure of (II).

Table 3. *Intra-annular torsion angles* (*ω*°) *for the non-aromatic rings in* (I) *and* (II)

1,2,4-Trioxane*

	ω° (I)	$\bar{\omega}$°†	*ω*° (II)
C(10)–O(1)–O(2)–C(3)	71·5 (3)	69·1 (7)	−84·6 (4)
O(1)–O(2)–C(3)–O(4)	−65·6 (3)	66·5 (17)	41·2 (4)
O(2)–C(3)–O(4)–C(5)	54·8 (3)	59·4 (19)	28·0 (5)
C(3)–O(4)–C(5)–C(10)	−45·9 (4)	51·1 (16)	−58·4 (5)
O(4)–C(5)–C(10)–O(1)	49·5 (3)	51·5 (19)	14·7 (4)
C(5)–C(10)–O(1)–O(2)	−62·3 (4)	60·6 (17)	49·9 (4)

Cyclohexadiene (I)		Cyclopentene (II)	
	ω(I)°		*ω*(II)°
C(9)–C(10)–C(5)–C(6)	43·9 (4)	C(8)–C(9)–C(5)–C(6)	15·7 (4)
C(10)–C(5)–C(6)–C(7)	−30·7 (3)	C(9)–C(5)–C(6)–C(7)	−10·9 (5)
C(5)–C(6)–C(7)–C(8)	2·1 (3)	C(5)–C(6)–C(7)–C(8)	1·3 (4)
C(6)–C(7)–C(8)–C(9)	12·8 (3)	C(6)–C(7)–C(8)–C(9)	9·2 (5)
C(7)–C(8)–C(9)–C(10)	3·7 (3)	C(7)–C(8)–C(9)–C(5)	−15·1 (4)
C(8)–C(9)–C(10)–C(5)	−32·1 (4)		

* For (II) read C(9) in place of C(10).

† Mean |*ω*| values for the six chair-form rings referenced in Table 4(*a*).

Table 4. *Condensed references to derivatives of* 1,2,4-*trioxane and* 1,2-*dioxane retrieved from the Cambridge Structural Database* (*CSD*)

CSD Refcode	Conf.[a]	Fused[b]	Coden	Vol.	Page	Year
(*a*) 1,2,4-Trioxane						
BHSPXD	C	*t*	JACSAT	96	2955	1974
COBMUB	C	*c*	HCACAV	67	1104	1984
IMNATX10	C	*n*	ACBCAR	33	3564	1977
Compound *A*[c]	C	*c*	HCACAV	67	2254	1984
Compound *B*[c]	C	*n*	TETRAB	41	2081	1985
(I)	C	*c*	This work			
QNGHSU	TB	*t*	SSBSEF	23	380	1980
(II)	TB	*c*	This work			
(*b*) 1,2-Dioxane						
BOJTUP	C	*n*	JCPKBH	–	1523	1982
BUDYII	C	*n*	JACSAT	105	1199	1983
OXBCHA	C	*n*	JACSAT	102	7574	1980
OXBCHB	C	*n*	JACSAT	102	7574	1980

(*a*) Conformation: C = chair, TB = twist boat.
(*b*) Fusion geometry: *c* = *cis*, *t* = *trans*, *n* = none.
(*c*) Structures not yet in CSD on 1 May 1985.

The twist-boat conformation adopted by the 1,2,4-trioxane in (II) is a result of geometrical constraints imposed by the *cis*-fused cyclopentene ring. The only other twist-boat 1,2,4-trioxane is in the antimalarial *Qinghaosu* (ASQRG, 1980). Here, however, the trioxane is part of a more complex bridged and fused ring assembly; the O—O torsion angle is low at 47·4° [84·6 (4)° in (II)] whilst the maximum angle of 75·1° is associated with O(2)—C(3).

The O—O bond lengths in (I) [1·467 (1) Å] and (II) [1·469 (2) Å] may be regarded as identical and are in excellent agreement with the mean value of 1·470 (2) Å for 43 cyclic Csp^3—O—O—Csp^3 fragments in structures with $R < 0{\cdot}07$ obtained from CSD (Allen *et al.*, 1979). The C—O distances in (I) and (II), however, show a wide range [1·401 (1)–1·444 (1) Å]. This is typical of the trioxanes of Table 4(*a*) where the C—O bonds range from 1·393 (18) to 1·466 (16) Å. Variability of C—O bond lengths has been discussed by Allen & Kirby (1984); in the current examples such distances will be heavily dependent on the electronic nature of the ring substituents.

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Structure of Synthetic (±)-Gephyrotoxin-223AB Hydrobromide*

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Abstract. 3-*n*-Butyl-5-*n*-propylperhydroindolizine hydrobromide, $C_{15}H_{30}N^+.Br^-$, $M_r = 304{\cdot}33$, monoclinic, $P2_1/c$, $a = 19{\cdot}299$ (4), $b = 12{\cdot}921$ (2), $c = 14{\cdot}263$ (3) Å, $\beta = 110{\cdot}86$ (1)°, $V = 3323{\cdot}5$ Å^3, $Z = 8$ with two molecules per asymmetric unit, $D_m = 1{\cdot}220$, $D_x = 1{\cdot}216$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha_1) = 1{\cdot}54056$ Å, $\mu = 3{\cdot}23$ mm^{-1}, $F(000) = 1296$, $T = 297$ K. $R = 0{\cdot}046$ for 3843 observed reflexions. The five-membered ring is in the N-envelope form, the six-membered ring has the chair conformation, and the ring junction is *trans*. The side chains in the two independent molecules show some significant conformational differences. Hydrogen bonds of the type N—H···Br···H—C link the molecules into chains parallel to **c**.

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