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(3*RS*,13*SR*)- and (3*RS*,13*RS*)-3-Bromoacetoxy-13-tetradecanolide,* $C_{16}H_{27}BrO_4$

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Abstract. $M_r = 363{\cdot}30$, triclinic, $P\bar{1}$, $Z = 2$, $F(000) = 380$, $T = 295$ K; (*RS,SR*) isomer: $a = 11{\cdot}546\,(4)$, $b = 14{\cdot}478\,(5)$, $c = 5{\cdot}283\,(2)$ Å, $\alpha = 92{\cdot}42\,(2)$, $\beta = 96{\cdot}93\,(2)$, $\gamma = 92{\cdot}81\,(2)°$, $V = 874{\cdot}6\,(6)$ Å^3, $D_x = 1{\cdot}380$ g cm^{-3}, Mo $K\alpha$, $\lambda(\alpha_1) = 0{\cdot}70930$ Å, $\mu = 22$ cm^{-1}, $R = 0{\cdot}054$ for 1101 reflections; (*RS,RS*) isomer: $a = 11{\cdot}868\,(3)$, $b = 13{\cdot}904\,(2)$, $c = 5{\cdot}482\,(1)$ Å, $\alpha = 90{\cdot}51\,(1)$, $\beta = 98{\cdot}82\,(1)$, $\gamma = 98{\cdot}48\,(1)°$, $V = 883{\cdot}7\,(3)$ Å^3, $D_x = 1{\cdot}365$ g cm^{-3}, Cu $K\alpha$, $\lambda(\alpha_1) = 1{\cdot}54056$ Å, $\mu = 31$ cm^{-1}, $R = 0{\cdot}057$ for 2394 reflections. The *S,R* (*cis*) isomer exists in 3344 and 3434 conformations (disordered in the crystal), while the *S,S* (*trans*) isomer has a 3335 conformation for the 14-membered ring; the bromoacetoxy and methyl substituents are equatorial. Molecular dimensions are generally close to normal values.

Introduction. The crystal structures of the title compounds† (Fig. 1) have been determined to assist in a study of the chemistry of the materials, and to obtain information on the conformations of the 14-membered rings.

Experimental. Colourless crystals, m.p. 343 K for the *cis* isomer [308–318 K for the *trans* isomer], dimensions $0{\cdot}13 \times 0{\cdot}04 \times 0{\cdot}28$ mm [$0{\cdot}12 \times 0{\cdot}04 \times 0{\cdot}38$ mm]; CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ [Cu $K\alpha$] radiation; cell parameters from $\sin\theta$ values of 24 reflections with $\theta = 11$–$22°$ [40–50°]; intensities for $\theta \le 24°$ [75°]; $h, k, l = -13$ to 13, -16 to 16, 0 to 6 [-14 to 14, -17 to 17, 0 to 6]; ω–2θ scan; ω-scan width $(1{\cdot}20 + 0{\cdot}35\tan\theta)°$ [$(0{\cdot}9 + 0{\cdot}14\tan\theta)°$] extended by 25% on each side of the peak for background measurement; horizontal aperture $(2 + \tan\theta)$ mm, vertical aperture 4 mm; ω-scan speed 1–10° min^{-1}; three standard reflections for intensity and orientation control; data scaled for slight decay in intensity and corrected for Lp and absorption (Busing & Levy, 1957; Coppens, Leiserowitz & Rabinovich, 1965), transmission factors 0·58–0·89 [0·41–0·80]. Of 2730 [3330] independent reflections, 1101 [2394] had $I \ge 3\sigma(I)$, where $\sigma^2(I) = S + 2B + [0{\cdot}04(S-B)]^2$, S = scan count, B = time-averaged background count. Structures solved by *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); refinement by full-matrix least squares on F (Sheldrick, 1976); $w = 1/\sigma^2(F)$; anisotropic thermal parameters; H atoms in calculated positions [difference map, isotropic refinement]; 0·6 e Å^{-3} in final difference maps near Br atoms; atomic scattering factors from Cromer & Mann (1968), Doyle & Turner (1968), and Stewart, Davidson & Simpson (1965); local adaptations of standard computer programs *ORFFE* (Busing, Martin & Levy, 1964), *ORTEP*II (Johnson, 1976), and *PLUTO* (Motherwell, 1978). The *cis* isomer exhibits disorder, with two half-occupied sites about 1 Å apart for each of C(6) and C(7); these atoms were refined with isotropic thermal parameters and occupancies constrained to total 1·0 (final values 0·51/0·49 and 0·52/0·48). The disorder must also extend to other atoms, particularly C(5) and C(8), but these atoms were treated as single sites and have slightly large thermal parameters. The *trans* isomer also probably exhibits slight disorder; the thermal parameters for O(4) correspond to an r.m.s. displacement of nearly 0·6 Å, but again this atom was refined as a single site. Final $R = 0{\cdot}054$, $wR = 0{\cdot}054$ for 1101 reflections (190 variables), $R = 0{\cdot}141$ for all 2730 reflections [$R = 0{\cdot}057$, $wR = 0{\cdot}058$ for 2394 reflections (190 scale and heavy atom parameters, 108 H parameters), $R = 0{\cdot}079$ for all 3300 reflections]. $(\Delta/\sigma)_{\max} = 0{\cdot}05$ [0·05].

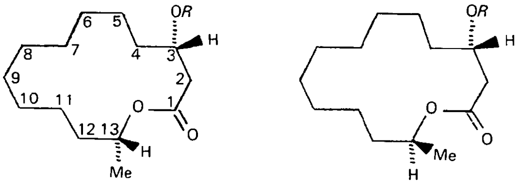

Fig. 1. 3-Bromoacetoxy-13-tetradecanolide: 3*S*,13*R* or *cis* isomer (left), 3*S*,13*S* or *trans* isomer (right).

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* Alternative names: (4*RS*,14*SR*)- and (4*RS*,14*RS*)-4-(bromoacetoxy)-14-methyl-1-oxacyclotetradecan-2-one.

† The materials are racemates; throughout this paper the 3*S*,13*R* (substituents '*cis*') and 3*S*,13*S* ('*trans*') diastereoisomers are depicted.

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Table 1. *Positional (fractional* × 10^4*) and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$)

$$U_{eq} = \tfrac{1}{3}\sum_i \sum_j U_{ij} a^*_i a^*_j \mathbf{a}_i . \mathbf{a}_j .$$

	cis				*trans*			
	x	y	z	U_{eq}	x	y	z	U_{eq}
Br	2387 (1)	1831 (1)	8020 (3)	95	1396 (1)	2524 (1)	7146 (2)	89
O(1)	797 (5)	7597 (4)	7693 (11)	53	4658 (3)	−1590 (3)	7776 (6)	58
O(2)	1056 (7)	6948 (5)	11450 (14)	82	3076 (3)	−1351 (3)	5232 (7)	69
O(3)	1596 (5)	4478 (4)	7347 (10)	54	1559 (3)	−255 (2)	7702 (6)	57
O(4)	2083 (6)	3685 (4)	10820 (14)	76	1431 (7)	771 (4)	10630 (9)	159
C(1)	940 (7)	6888 (7)	9164 (22)	46	3613 (4)	−1313 (3)	7268 (10)	45
C(2)	898 (7)	5987 (6)	7573 (17)	45	3260 (5)	−924 (4)	9548 (9)	47
C(3)	1772 (8)	5346 (6)	8874 (18)	52	1971 (5)	−965 (4)	9473 (10)	49
C(4)	3037 (9)	5680 (6)	9021 (19)	66	1243 (5)	−1929 (4)	8687 (12)	57
C(5)	3496 (8)	5899 (9)	6455 (23)	112	1503 (6)	−2748 (4)	10452 (12)	61
C(6)†	4719 (11)	6359 (13)	7552 (37)	62	844 (6)	−3739 (5)	9493 (14)	73
C(7)†	5290 (15)	6926 (11)	5541 (46)	68	1385 (7)	−4205 (5)	7531 (14)	78
C(8)	4479 (10)	7753 (7)	5260 (25)	118	2400 (7)	−4716 (5)	8583 (14)	78
C(9)	4568 (9)	8621 (8)	7121 (23)	98	3110 (8)	−4992 (5)	6711 (16)	86
C(10)	3744 (11)	9368 (8)	6434 (23)	90	3879 (7)	−4135 (5)	5784 (15)	77
C(11)	2445 (9)	9109 (7)	6373 (22)	72	4869 (8)	−3656 (6)	7689 (16)	81
C(12)	2089 (10)	8948 (7)	8987 (20)	64	5690 (6)	−2857 (5)	6753 (15)	75
C(13)	843 (10)	8530 (6)	8881 (18)	59	5120 (5)	−2003 (4)	5715 (11)	58
C(14)	−76 (9)	9038 (7)	7351 (20)	74	5925 (8)	−1207 (6)	4731 (18)	80
C(15)	1825 (7)	3701 (6)	8569 (23)	47	1332 (5)	560 (4)	8584 (11)	60
C(16)	1669 (8)	2909 (6)	6633 (19)	55	895 (6)	1164 (4)	6445 (11)	57
C(6′)†	4875 (11)	6035 (11)	5880 (40)	62				
C(7′)†	5067 (20)	7037 (10)	7062 (39)	68				

† Occupancy = 0·5 in the *cis* compound.

Table 2. *Ring torsion angles* (°) ($\sigma = 0{\cdot}4$–$1{\cdot}4$°)

	cis				*trans*	
	Obs. (6,7)	Ideal 3344	Obs. (6′,7′)	Ideal 3434	Obs.	Ideal 3335
C(3)—C(4)	−56	−55	−56	−60	63	55
C(4)—C(5)	171	170	−165	180	−174	180
C(5)—C(6)	−163	−165	−77	−60	79	75
C(6)—C(7)	69	65	−76	−60	81	80
C(7)—C(8)	81	60	164	180	−167	180
C(8)—C(9)	177	180	−159	180	73	80
C(9)—C(10)	64	75	64	60	68	75
C(10)—C(11)	69	75	69	60	176	180
C(11)—C(12)	−170	180	−170	180	60	55
C(12)—C(13)	66	60	66	60	61	70
C(13)—O(1)	94	65	94	60	−139	−155
O(1)—C(1)	−178	−165	−178	180	179	160
C(1)—C(2)	144	170	144	180	−157	−155
C(2)—C(3)	−65	−55	−65	−60	50	70

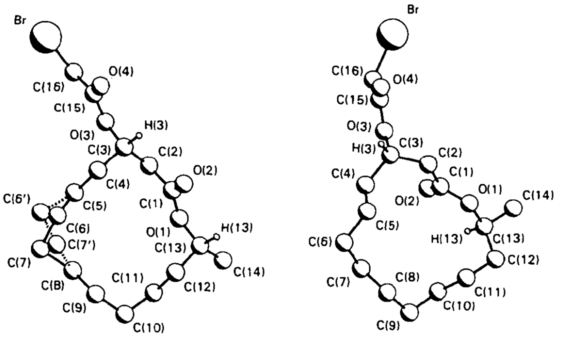

Fig. 2. Views of the *cis* (left) and *trans* (right) isomers; H(3) and H(13) are the only H atoms shown.

Table 3. *Bond lengths* (Å) *and angles* (°)

	cis	*trans*
C(1)—C(2)	1·517 (14)	1·499 (8)
C(2)—C(3)	1·527 (12)	1·517 (8)
C(3)—C(4)	1·508 (14)	1·504 (7)
C(4)—C(5)	1·553 (16)	1·536 (9)
C(5)—C(6)	1·566 (17), 1·559 (17)	1·526 (8)
C(6)—C(7)	1·558 (29), 1·558 (22)	1·520 (12)
C(7)—C(8)	1·557 (20), 1·561 (22)	1·528 (12)
C(8)—C(9)	1·554 (16)	1·505 (13)
C(9)—C(10)	1·502 (17)	1·531 (11)
C(10)—C(11)	1·524 (16)	1·515 (11)
C(11)—C(12)	1·512 (16)	1·514 (11)
C(12)—C(13)	1·527 (16)	1·524 (9)
C(13)—O(1)	1·461 (10)	1·476 (7)
O(1)—C(1)	1·318 (12)	1·342 (6)
C(1)—O(2)	1·198 (14)	1·194 (6)
C(3)—O(3)	1·456 (10)	1·473 (6)
O(3)—C(15)	1·342 (11)	1·308 (7)
C(15)—O(4)	1·192 (14)	1·141 (8)
C(15)—C(16)	1·493 (14)	1·519 (8)
C(16)—Br	1·933 (9)	1·914 (6)
C(13)—C(14)	1·497 (14)	1·512 (11)
O(1)—C(1)—C(2)	110·9 (9)	111·0 (4)
O(1)—C(1)—O(2)	124·3 (9)	123·0 (5)
C(2)—C(1)—O(2)	124·8 (9)	126·0 (5)
C(1)—C(2)—C(3)	109·1 (7)	115·2 (4)
C(2)—C(3)—C(4)	115·2 (8)	116·0 (5)
C(2)—C(3)—O(3)	105·1 (7)	108·8 (4)
C(4)—C(3)—O(3)	108·8 (7)	106·3 (4)
C(3)—C(4)—C(5)	116·6 (8)	113·3 (5)
C(4)—C(5)—C(6)	98·5 (10), 128·7 (11)	112·5 (5)
C(5)—C(6)—C(7)	112·4 (14), 99·1 (14)	113·3 (6)
C(6)—C(7)—C(8)	101·2 (14), 110·2 (14)	113·7 (6)
C(7)—C(8)—C(9)	124·9 (12), 100·3 (11)	114·8 (7)
C(8)—C(9)—C(10)	116·7 (9)	114·5 (6)
C(9)—C(10)—C(11)	116·5 (10)	114·9 (7)
C(10)—C(11)—C(12)	113·1 (9)	115·6 (7)
C(11)—C(12)—C(13)	112·9 (8)	113·9 (6)
C(12)—C(13)—O(1)	108·4 (8)	106·1 (5)
C(12)—C(13)—C(14)	115·4 (8)	114·5 (6)
O(1)—C(13)—C(14)	106·2 (7)	108·5 (5)
C(13)—O(1)—C(1)	119·0 (7)	117·4 (4)
C(3)—O(3)—C(15)	116·8 (7)	118·0 (4)
O(3)—C(15)—C(16)	107·9 (9)	108·9 (5)
O(3)—C(15)—O(4)	123·6 (8)	125·2 (6)
C(16)—C(15)—O(4)	128·5 (9)	125·9 (6)
C(15)—C(16)—Br	110·5 (7)	111·3 (4)

Discussion. Final atomic parameters are in Table 1,* ring torsion angles in Table 2, and interatomic distances and angles in Table 3.

Both isomers contain 14-membered rings (Fig. 2). The *cis* isomer exhibits equal amounts of 3344 {for C(6), C(7)} and 3434 {for C(6′), C(7′)} conformations;† the conformation of the *trans* isomer is 3335. The bends occur at different atoms in the two isomers: at C(3), C(7) {or C(6′)}, C(10), and C(13) in the *cis* isomer, but at C(3), C(6), C(9), and C(12) in the *trans* isomer. The observed torsion angles (Table 2) are closely similar to those predicted for the three lowest-energy conformations of a 14-membered ring (Dale, 1973). The conformations are probably partly controlled by the tendency of the bulky 3-bromoacetoxy and 13-methyl substituents to occupy less-sterically-hindered equatorial sites. In the *cis* isomer this results in the C=O(2) and C=O(4) bonds being approximately parallel, while the configurational difference at C(13) in the *trans* isomer causes a conformational change which results in C=O(2) and C=O(4) being approximately antiparallel.

Bond lengths and angles (Table 3) are generally within normal ranges. The slight (though not statistically significant) elongations of the C—C bonds involving C(6) and C(7) in the *cis* isomer probably result from errors due to the disorder, as do the apparently anomalous angles in this region. The short value observed for the length of the C=O(4) bond in the *trans* compound is probably affected by error due to disorder or to large thermal libration.

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* Anisotropic thermal parameters, H parameters, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42134 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† The nomenclature is that of Dale (1973), the numbers indicating the numbers of bonds in the straight-chain portions of the rings.

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Structure of 10-Methylphenothiazine 5-Oxide, $C_{13}H_{11}NOS$

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Abstract. $M_r = 229{\cdot}30$, monoclinic, $P2_1/n$, $a = 11{\cdot}289\,(2)$, $b = 10{\cdot}831\,(3)$, $c = 8{\cdot}818\,(2)$ Å, $\beta = 91{\cdot}80\,(2)°$, $V = 1077{\cdot}7\,(5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}413$, $D_m = 1{\cdot}42$ g cm^{-3} (by flotation), λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 2{\cdot}27$ cm^{-1}, $F(000) = 480$, $T = 294$ K, final $R = 0{\cdot}044$ for 1980 observed reflections. The 10-methyl group is in a 'boat-equatorial' and the sulfinyl oxygen is in a 'boat-axial' conformation with respect to the central ring of the phenothiazine ring system. The folding angle between the least-squares planes of the two benzo rings is 151·2 (8)°.

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