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5-*exo*-Bromo- and 5-*exo*-Iodo-6-*endo*-norbornanol-2-*endo*-carboxylic Acid Lactones

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Abstract. $C_8H_9O_2Br$, monoclinic, $P2_1/c$, $a=6{\cdot}383$ (4), $b=11{\cdot}180$ (6), $c=11{\cdot}430$ (7) Å, $\beta=95{\cdot}76$ (3)°, $Z=4$, $D_c=1{\cdot}78$, $D_m=1{\cdot}76$ (2) g cm^{-3}. $C_8H_9O_2I$, orthorhombic, $Pbca$, $a=11{\cdot}825$ (6), $b=15{\cdot}609$ (25), $c=11{\cdot}310$ (7) Å, $Z=16$, $D_c=2{\cdot}05$, $D_m=2{\cdot}11$ (5) g cm^{-3}. The bromolactone, and both independent molecules of the iodolactone, exist in the 2,6-bridged configuration with normal bond lengths. The bond angles, however, show considerable departure from their ideal values. The angle at the bridging carbon atom is 94·8 (4)° for the bromolactone and 103 (2) and 101 (2)° for the two molecules of iodolactone.

Introduction. For the bromolactone, a crystal of dimensions 0·58 × 0·35 × 0·08 mm was used. The data showed systematic absences of $l=2n+1$ for $h0l$ and $k=2n+1$ for $0k0$; the linear absorption coefficient $\mu=53{\cdot}07$ cm^{-1} for Mo $K\alpha$ radiation. For the iodolactone, a crystal of dimensions 0·60 × 0·04 × 0·47 mm was used. The systematic absences were $k=2n+1$ for $0kl$, $l=2n+1$ for $h0l$, and $h=2n+1$ for $hk0$; $\mu=37{\cdot}17$ cm^{-1} for Mo $K\alpha$ radiation. All diffraction measurements were made with Mo $K\alpha$ radiation on a 4-circle Picker automatic diffractometer with a scintillation counter and a pulse-height analyzer. For the bromolactone the incident beam was filtered to remove the β-radiation by interposing a niobium foil of thickness 3·0 mil between the incident beam and the crystal. For the iodolactone a graphite monochromator was used for this purpose. The cell constants were determined by the least-squares procedure of Busing & Levy (1967). Both intensity data sets were corrected for crystal decomposition, background and Lorentz-polarization factors. Absorption corrections were applied using Hamilton's *GONO* 9 program. The transmission factors for the bromolactone ranged from 0·205 (for $\bar{5}10$) to 0·707 (for $\bar{5}24$) and those for the iodolactone from 0·413 (for 230) to 0·760 (for 10,0,2). A total of 1440 reflections [$912>3\sigma(I)$] for the bromo- and 2360 reflections [$1458>1{\cdot}5\sigma(I)$] for the iodolactone were measured.

Both structures were solved by standard heavy-atom techniques using our version of Zalkin's *FORDAP* Fourier program. The hydrogen atoms of the iodolactone crystal could not be located. They were, therefore, placed in their theoretical positions 0·95 Å away from the attached carbon atoms and not refined. The hydrogens of the bromolactone crystal were located from a difference Fourier synthesis and refined with isotropic temperature parameters. All other atoms in the structures were refined with anisotropic temperature parameters. The refinements were carried out using J. A. Ibers's full-matrix least-squares program *NUCLS*, the function minimized being $\sum w(|F_o|-|F_c|)^2$ $|F_c|)^2$; the weights w were taken as $4F_o^2/\sigma^2(F_o)^2$.

Examination of the data revealed that secondary extinction was significant for the iodolactone since for strong low-order reflections $|F_o|$ was systematically smaller than $|F_c|$. An extinction correction of the form

$$F_o^{\text{corr}}=F_o[c\beta(\theta)I+(1+c^2\beta^2(\theta)I^2)^{1/2}]^{1/2}\,,$$

which is strictly valid for a spherical crystal (Zachariasen, 1968) was, therefore, applied. The function minimized in the least-squares procedure for the iodo-

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Table 1. *Positional and thermal parameters for the bromolactone*, $C_8H_9O_2Br$

Hydrogen atom positional parameters are × 10^3. Parameters for other atoms are all × 10^4.
The form of the anisotropic thermal ellipsoid is $\exp\{-[\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl]\}$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	−2403 (1)	5514 (1)	3981 (1)	347 (2)	103 (1)	99 (1)	11 (1)	−3 (1)	−17 (1)
C(1)	−2865 (8)	2633 (5)	2261 (5)	197 (15)	75 (5)	83 (5)	−9 (7)	10 (7)	18 (4)
C(2)	−2852 (8)	2734 (5)	937 (5)	138 (14)	81 (5)	86 (5)	13 (7)	22 (6)	−3 (4)
C(3)	−1277 (10)	3779 (7)	813 (6)	134 (16)	126 (8)	102 (6)	8 (9)	57 (8)	−3 (6)
C(4)	−781 (8)	4204 (5)	2083 (5)	106 (13)	91 (5)	99 (6)	−10 (7)	28 (6)	0 (4)
C(5)	−2802 (8)	4771 (5)	2424 (5)	170 (14)	68 (5)	80 (5)	17 (7)	10 (6)	10 (4)
C(6)	−4302 (8)	397 (5)	2430 (5)	151 (14)	94 (5)	66 (5)	9 (7)	32 (7)	8 (4)
C(7)	−700 (9)	3060 (5)	2773 (6)	178 (16)	96 (6)	102 (7)	45 (8)	−1 (8)	−1 (5)
C(8)	−5020 (8)	3160 (5)	514 (5)	186 (15)	81 (5)	80 (5)	−21 (7)	23 (7)	8 (4)
O(1)	−5821 (5)	3738 (3)	1405 (3)	114 (9)	114 (4)	85 (3)	20 (5)	7 (4)	−1 (3)
O(2)	4008 (6)	3084 (4)	−433 (3)	279 (12)	125 (4)	72 (3)	−13 (6)	−7 (5)	9 (3)

Table 1 (*cont.*)

	x	y	z	B (Å^2)
H(1)	−334 (8)	190 (5)	256 (4)	4 (1)
H(2)	−262 (8)	202 (5)	56 (5)	4 (1)
H(31)	−196 (9)	444 (5)	24 (5)	5 (1)
H(32)	−36 (7)	347 (4)	63 (4)	2 (1)
H(4)	44 (9)	482 (5)	221 (4)	5 (1)
H(5)	332 (8)	37 (4)	306 (4)	3 (1)
H(6)	−493 (7)	363 (4)	300 (4)	3 (1)
H(71)	−65 (8)	317 (4)	367 (5)	5 (1)
H(72)	23 (8)	259 (5)	255 (4)	4 (1)

lactone was now $\sum w(|F_o|-|F_c|/g)^2$, where $g=[c\beta(\theta)I+(1+c^2\beta^2(\theta)I^2)^{1/2}]^{1/2}$, c is the extinction coefficient, I the corrected intensity, and $\beta(\theta)$ is the function described by Zachariasen (1963). The final refined value of the extinction coefficient, c, is 6·1 (11) × 10^{-7}.

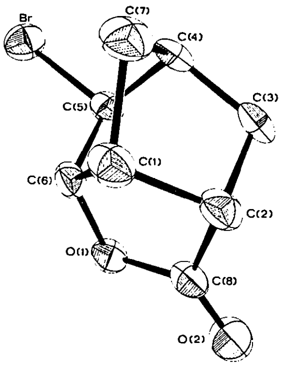

Fig. 1. View of the bromolactone molecule, showing the numbering scheme and demonstrating that the molecule has the 2,6-bridged configuration. Thermal ellipsoids are at the 40% probability level, and hydrogen atoms are omitted for clarity.

The final agreement indices, $R=\sum||F_o-F_c||/\sum|F_o|$ and $R_w=[\sum(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$, for the two structures are: bromolactone, $R=0·036$, $R_w=0·044$; iodolactone, $R=0·074$, $R_w=0·070$.

The positional and thermal parameters derived from the last cycle of least-squares refinement, with their associated standard deviations as estimated from the inverse matrix, are given in Tables 1 and 2 for the bromolactone and the iodolactone respectively. The observed and calculated structure amplitudes are available.*

Discussion. The halolactones obtained from the bromination (Roberts, Trumbull, Bennett & Armstrong, 1950) or iodination (Ver Nooy & Rondestvedt, 1955) of 5-norbornene-2-*endo*-carboxylic acid have assumed a central role in the spectral and structural correlations of many norbornyl derivatives (Crundwell & Templeton, 1964; Ramey, Lini, Moriarty, Gopal & Welsh, 1967; Ford, Kitching & Wells, 1969; Beckmann & Geiger, 1961; Beckmann, Eder & Geiger, 1969). Initially the 2,6-bridged structure was assumed for these compounds, without any apparent justification.

More recently, there has been disagreement as to whether the 2,6-bridged structure or the 2,5-bridged structure properly represents the iodolactone (Risinger, Green & Green, 1969; Crundwell, Farmer & Kofi-Tsekpo, 1969; Oxer & Wege, 1969). Our structural results show that both compounds exist in the 2,6-bridged configuration in the solid state. The structure of the bromelactone is shown in Fig. 1.

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Table 2. *Positional and thermal parameters for the iodolactone*, $C_8H_9O_2I$

Values are × 10^4.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I(1)	894 (1)	899 (1)	−104 (1)	92 (1)	23 (0)	129 (1)	14 (1)	−18 (1)	3 (1)
I(2)	3339 (1)	3724 (1)	2159 (1)	89 (1)	22 (0)	143 (2)	−10 (1)	−8 (1)	0 (1)
C(1)	2794 (18)	279 (8)	2511 (16)	120 (21)	16 (4)	150 (26)	5 (8)	83 (18)	10 (8)
C(2)	4064 (16)	282 (8)	2259 (14)	117 (21)	21 (4)	76 (16)	12 (8)	−36 (16)	0 (7)
C(3)	4177 (16)	776 (7)	1595 (17)	104 (20)	14 (4)	177 (23)	3 (8)	8 (18)	3 (8)
C(4)	3064 (15)	1020 (6)	1490 (19)	89 (19)	6 (3)	218 (28)	−1 (6)	15 (20)	12 (7)
C(5)	2640 (20)	601 (8)	447 (18)	256 (33)	16 (4)	131 (22)	−42 (10)	−0 (23)	16 (8)
O(6)	2391 (18)	183 (10)	1096 (16)	145 (23)	40 (7)	105 (22)	−31 (11)	28 (18)	−16 (10)
C(7)	2394 (17)	804 (11)	2419 (16)	107 (21)	46 (7)	108 (20)	44 (11)	7 (17)	10 (10)
C(8)	4255 (16)	−180 (7)	1462 (15)	87 (18)	18 (4)	89 (18)	−2 (8)	−17 (17)	15 (8)
O(1)	3399 (12)	−210 (4)	680 (11)	165 (16)	19 (3)	159 (14)	40 (6)	−45 (15)	−23 (5)
O(2)	4978 (11)	−490 (6)	1395 (12)	130 (15)	26 (3)	186 (18)	35 (6)	6 (13)	−6 (6)
C(10)	1945 (19)	2523 (8)	380 (18)	140 (26)	18 (4)	148 (25)	24 (9)	14 (19)	9 (8)
C(20)	652 (18)	2530 (8)	3697 (15)	134 (23)	16 (4)	120 (21)	−12 (8)	−53 (17)	2 (7)
C(30)	429 (16)	3096 (8)	259 (14)	129 (21)	24 (5)	102 (19)	7 (8)	−2 (15)	10 (8)
C(40)	1539 (17)	3369 (6)	360 (18)	111 (20)	5 (3)	194 (27)	−8 (7)	−9 (19)	3 (7)
C(50)	1823 (19)	3273 (9)	1678 (15)	210 (28)	27 (5)	84 (19)	6 (11)	−69 (19)	9 (8)
C(60)	2100 (16)	2736 (12)	1714 (20)	84 (19)	51 (8)	181 (32)	21 (11)	−16 (19)	57 (14)
C(70)	2291 (19)	3018 (11)	−185 (19)	131 (25)	35 (7)	199 (29)	2 (11)	55 (21)	−13 (12)
C(80)	276 (20)	2339 (8)	1619 (17)	133 (25)	20 (5)	104 (22)	−12 (9)	−1 (21)	8 (8)
O(10)	1084 (16)	2472 (8)	2345 (12)	243 (23)	73 (6)	131 (15)	−99 (11)	−100 (17)	61 (8)
O(20)	−493 (13)	2097 (6)	1917 (14)	143 (17)	34 (4)	214 (20)	−45 (7)	11 (14)	13 (7)

The bond lengths and angles not involving the hydrogen atoms for the bromolactone and the two independent molecules of iodolactone are presented in Table 3. The nine C–H bond lengths in the bromolactone ranged from 0·73 to 1·06 Å with an average estimated standard deviation of 0·05 Å, and bond angles involving the hydrogen atoms ranged from 102 to 120° with an average estimated standard deviation of 5°. No bond lengths or angles involving H atoms are reported for iodolactone since they could not be located in a difference Fourier synthesis.

Table 3. *Bond lengths* (Å) *and angles* (°) *and their estimated standard deviations* (*in parentheses*) *for the bromolactone and the two independent molecules of iodolactone, not involving hydrogen atoms*

X = Br or I.

	Bromo-lactone	Iodo-lactone 1	Iodo-lactone 2
C(5)–X	1·957 (6)	2·29 (3)	2·20 (2)
C(1)–C(2)	1·518 (8)	1·53 (2)	1·53 (3)
C(2)–C(3)	1·557 (8)	1·48 (2)	1·48 (3)
C(3)–C(4)	1·530 (8)	1·46 (2)	1·49 (2)
C(4)–C(5)	1·522 (7)	1·67 (3)	1·55 (2)
C(5)–C(6)	1·537 (7)	1·33 (3)	1·41 (3)
C(6)–C(1)	1·526 (7)	1·69 (3)	1·61 (3)
C(1)–C(7)	1·522 (8)	1·43 (3)	1·48 (3)
C(4)–C(7)	1·500 (8)	1·43 (3)	1·41 (3)
C(2)–C(8)	1·496 (7)	1·50 (2)	1·53 (2)
C(8)–O(1)	1·350 (6)	1·35 (2)	1·30 (2)
C(6)–O(1)	1·445 (6)	1·63 (2)	1·55 (2)
C(8)–O(2)	1·196 (6)	1·17 (2)	1·15 (2)
X——C(5)–C(4)	111·9 (4)	104 (1)	109 (1)
X——C(5)–C(6)	110·6 (4)	103 (2)	108 (2)
C(4)–C(5)–C(6)	102·7 (4)	101 (2)	104 (2)
C(5)–C(6)–C(1)	103·0 (4)	110 (2)	106 (2)
C(5)–C(6)–O(1)	109·8 (4)	100 (2)	105 (2)
C(1)–C(6)–O(1)	106·6 (4)	99 (2)	101 (2)
C(6)–C(1)–C(7)	103·9 (5)	89 (2)	95 (2)
C(6)–C(1)–C(2)	97·5 (4)	96 (1)	96 (2)
C(2)–C(1)–C(7)	105·3 (5)	108 (2)	106 (2)
C(1)–C(2)–C(3)	102·4 (5)	101 (2)	101 (2)
C(1)–C(2)–C(8)	104·4 (4)	105 (2)	107 (2)
C(3)–C(2)–C(8)	108·5 (5)	111 (2)	111 (2)
C(2)–C(3)–C(4)	102·7 (5)	109 (2)	107 (2)
C(3)–C(4)–C(5)	105·8 (5)	93 (2)	101 (2)
C(3)–C(4)–C(7)	103·1 (5)	106 (2)	103 (2)
C(5)–C(4)–C(7)	101·9 (5)	96 (2)	101 (2)
C(1)–C(7)–C(4)	94·8 (4)	103 (2)	101 (2)
C(2)–C(8)–O(1)	108·5 (5)	109 (2)	106 (2)
C(2)–C(8)–O(2)	130·5 (6)	133 (2)	132 (2)
O(1)–C(8)–O(2)	121·0 (5)	118 (2)	122 (2)
C(6)–O(1)–C(8)	108·8 (4)	109 (1)	113 (2)

Since it was not possible to obtain good bond lengths and angles for the iodolactone all the discussions which follow are based on the more precisely determined structure of the bromolactone, unless stated otherwise. All the bond angles in the bicycloheptane moiety have values considerably less than the normal 109·5°. Values similar to these have been obtained for related compounds by others (Macdonald & Trotter, 1965; Fratini, Britts & Karle, 1967; Flippen, 1972).

The most constrained angle in the molecule is that at the bridge carbon atom C(7), namely, C(1)–C(7)–C(4), which has the value 94·8°. Authors quoted above have found values of 97, 96, 94, and 96°, respectively, for this angle. It is interesting to note that the angle C(2)–C(1)–C(6) at the bridgehead carbon C(1) in this compound of 97·5° is very similar to the value of 97·8° found in the 7-acetoxylactone (Flippen, 1972); these values are considerably smaller than those in the other structures [Macdonald & Trotter, 1965 (104, 105°); Fratini, Britts & Karle, 1967 (111°)]. This is presumably due to the extra strain introduced by the formation of the lactone ring. The similar angle C(3)–C(4)–C(5) at the other bridgehead carbon C(4) is only slightly smaller (105·8°) than the tetrahedral value in the bromo lactone, and is close to tetrahedral (109·7°) in the 7-acetoxy lactone. Similar values have been reported for this angle in other molecules with the norbornane moiety but lacking the lactone ring. The effect of the lactone ring formation is, therefore, seen only at the carbon atom C(1) and not at C(4). The three angles around C(8) are all different from each other but agree quite well with those reported for the corresponding angles for the 7-acetoxylactone.

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