The Crystal and Molecular Structure of Racemic 3-Bromo-4,4-dihydroxypimelic Acid Dilactone

LOTTE BREHM*

Chemical Laboratory C, The Royal Danish School of Pharmacy, Copenhagen, Denmark

Racemic 3-bromo-4,4-dihydroxypimelic acid dilactone, $C_7H_7O_4Br$, crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the asymmetric unit, and with unit-cell dimensions a=12.942(6), b=14.17(1), c=9.15(1) Å and $\beta=102.1(1)^\circ$. The structure was solved using conventional heavy atom techniques. Full matrix least-squares refinement with anisotropic temperature factors for the bromine atoms gave an R index of 0.145 for 1494 photographic data. The two molecules per asymmetric unit appear to be identical.

In an attempt in this laboratory ¹ to synthesize 2,6-dibromo-4-ketopimelic acid, 4,4-dihydroxypimelic acid dilactone was treated with bromine while being irradiated with UV-light. The only substance to be isolated was a monobromo-4,4-dihydroxypimelic acid dilactone which has not been previously reported.

The crystal and molecular structure of this compound have been elucidated

by an X-ray analysis which is described in the following section.

Single crystals of the compound suitable for diffraction studies were formed from 96 % ethanol as elongated monoclinic needles, m.p. $106-107^{\circ}$. Specimens no larger than 0.2 mm in cross section were used. Weissenberg photographs indicated unambiguously that the space group of the crystals is $P2_1/c$, the systematically absent reflections being: h0l when l is odd and 0k0 when k is odd. Unit cell dimensions are a=12.942(6), b=14.17(1), c=9.15(1) Å, and $\beta=102.1(1)^{\circ}$. The observed density, measured by flotation in zinc bromide solution, is $1.92 \text{ g} \cdot \text{cm}^{-3}$; the theoretical density calculated on the basis of eight molecules per unit cell (two per asymmetric unit) is $1.902 \text{ g} \cdot \text{cm}^{-3}$. The direction of crystal elongation is parallel to c. Multiple-film equi-inclination Weissenberg photographs were taken of levels hkl for $0 \le L \le 6$ and hkl for $0 \le k \le 10$ using $CuK\alpha$ radiation ($\lambda=1.5418$ Å). The intensities of the diffraction maxima were measured on a Flying-spot Integrating Microdensitometer (Joyce-Loebl

^{*} Present address: Chemical Crystallography Laboratory, South Parks Road, University of Oxford, Oxford, England.

and Co.). After corrections for Lorentz and polarization factors the observations were brought to a common relative scale using the least-squares method of Hamilton, Rollett and Sparks, 1965.2 No corrections were made for

Table 1. Final position and thermal parameters. Estimated standard deviations ($\times 10^4$) are in parentheses.

Atomic pos	itions	x/a		y/b		z/c	
$\operatorname{Br}(1)$		0.4372(2)		0.1574(2)		66(3)	
O(1)		0.5309(15)	_	-0.0651(13)	0.33	40(20)	
O(2)		0.6330(11)		0.0255(10)	0.22	37(15)	
O(3)		0.7252(12)		0.1572(10)	0.3115(16)		
O(4)		0.8960(14)		0.1920(13)	0.3545(19)		
C(1)		0.5545(17)		0.0132(16)	0.30	15(23)	
C(2)		0.5094(23)		0.1086(21)	0.33	50(31)	
C(3)		0.5402(21)		0.1724(18)	0.21	63(29)	
C(4)		0.6463(17)		0.1238(17)	0.19	0 5(23)	
C(5)		0.6851(17)		0.1374(16)	0.04	96(23)	
$\mathbf{C}(6)$		0.8022(21)		0.1393(20)	0.10	48(29)	
C(7)		0.8195(17)		0.1690(15)	0.26	74(24)	
Br(1')		0.1062(2)		0.0809(2)		38(2)	
O(1')		0.2852(15)		-0.1448(13)	0.34	06(20)	
O(2')		0.2592(11)	_	-0.0016(10)		59(14)	
O(3')		0.1369(12)		0.0395(11)	0.56	14(16)	
O(4')		0.1506(14)		0.1007(12)		96(19)	
$\mathbf{C}(\mathbf{1'})$		0.2224(15)	-	-0.0820(15)	0.356	0 9 (20)	
$\mathbf{C}(\mathbf{2'})$		0.1091(19)	_	-0.0820(18)		63(25)	
C(3')		0.0849(16)		0.0242(14)	0.30	15(20)	
C(4')		0.1720(15)		0.0610(12)	0.42	57(19)	
C(5')		0.2059(18)		0.1606(16)	0.44	20(24)	
C(6')		0.2415(21)		0.1784(18)		39(28)	
C(7')		0.1723(17)		0.1082(15)		85(22)	
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Thermal parameters Anisotropic T=exp[$-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)$]							
	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4 eta_{33}$	$10^4 \beta_{12}$	$10^4 \beta_{13}$	$10^4 eta_{23}$	
Br(1)	60(2)	55(2)	119(4)	17(2)	-21(2)	-12(2)	
$\mathbf{Br}(\mathbf{1'})$	67(2)	42(2)	4 8(3)	-16(1)	2(2)	8(2)	
Isotropic	$T = \exp[-$	$-\mathbf{B}(\sin\! heta/\lambda)^2]$					
		B (e.s.d. $\times10)$			B (e.s.d	.×10)	
O(1)		3.2(3)		O(1')	3.3(3)	
O(2)		1.6(3)		O(2')	1.5	2)	
O(3)		1.8(2)		O(3')	1.7(3)	
O(4)		2.8(3)		O(4')	3.1	3)	
C(1)		2.0(4)		$\mathbf{C}(\mathbf{1'})$	1.1(3)	
C(2)		3.5(5)		C(2')	2.2(
C(3)		2.5(5)	C(3') 1.2(3)				
C(4)		1.7(4)		C(4')	0.9		
C(5)		1.8(4)		C(5')	1.7	4)	
C(6)		3.1(5)		C(6')	2.80		
C(7)		1.6(4)		C(7')	1.7((4)	

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extinction or absorption (the linear absorption coefficient, $\mu = 75$ cm⁻¹). Since the intensities decrease rapidly with increasing diffraction angle the total number of observed independent non-zero data was only 1494, that is, about

50 % of the total within the sphere of reflexion.

The atomic coordinates of the bromine atoms were deduced from a three-dimensional Patterson function and a three-dimensional electron density map phased only on the contributions of the bromine atoms gave positions for all other non-hydrogen atoms. The coordinates of all the postulated atoms and an overall temperature factor were partially refined by the Fourier method (final R index 0.25). The refinement was then completed using the full-matrix least-squares method. Anisotropic temperature factors for the bromine atoms and individual isotropic factors for the other atoms were varied with the coordinates and the data scale factor. The data weighting scheme of Cruickshank was used. The final R index is 0.145. Final position and thermal parameters, and bond angles with standard deviations are listed in Tables 1 and 2, respectively, while the final bond lengths with standard deviations are shown in Fig. 1a and b.

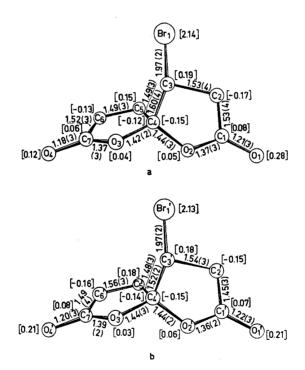


Fig. 1. Bond lengths (Å) of each of the two crystallographically independent molecules a and b in the asymmetric unit. Their estimated standard deviations are in parentheses. The distance (Å) of each atom from the least-squares plane calculated through the ring in which the atoms are situated or to which they are bonded, is shown in square brackets adjacent to the atom.

Table 2. Bond angles (°). Estimated standard deviations are in parentheses.

O(1)-C(1)-C(2)	130(2)
O(1) - C(1) - O(2)	120(2)
O(2) - C(1) - C(2)	110(2)
O(2)-C(1)-C(2) C(1)-C(2)-C(3)	
C(1) - C(2) - C(3)	102(2)
C(2) - C(3) - C(4)	102(2)
C(2) - C(3) - Br(1)	110(2)
C(4)-C(3)-Br(1) C(3)-C(4)-O(2)	106(2)
C(3)-C(4)-C(2)	104(2)
C(4)-C(2)-C(1)	112(2)
C(3)-C(4)-C(5)	122(2)
O(2) - C(4) - O(3)	105(2)
C(5)-C(4)-O(2) C(3)-C(4)-O(3)	113(2)
C(3) - C(4) - O(3)	104(2)
O(3)-C(4)-C(5)	108(2)
C(4)-C(5)-C(6)	102(2)
	106(2)
C(5)-C(6)-C(7) C(6)-C(7)-C(3)	107(2)
C(6)-C(7)-O(4)	132(2)
O(4) - C(7) - O(3)	121(2)
C(7) - O(3) - C(4)	111(2)
O(1) - O(0) - O(1)	111(2)
0/1/\ 0/1/\ 0/9/\	199/9\
O(1') - C(1') - C(2')	128(2)
O(1')-C(1')-O(2')	119(2)
O(1')-C(1')-O(2') O(2')-C(1')-C(2')	119(2) 113(2)
O(1')-C(1')-O(2') O(2')-C(1')-C(2') C(1')-C(2')-C(3')	119(2) 113(2) 101(2)
O(1')-C(1')-O(2') O(2')-C(1')-C(2') C(1')-C(2')-C(3') C(2')-C(3')-C(4')	119(2) 113(2) 101(2) 104(2)
O(1')-C(1')-O(2') O(2')-C(1')-C(2') C(1')-C(2')-C(3') C(2')-C(3')-C(4') C(2')-C(3')-Br(1')	119(2) 113(2) 101(2) 104(2) 108(1)
$\begin{array}{c} O(1') - C(1') - O(2') \\ O(2') - C(1') - C(2') \\ C(1') - C(2') - C(3') \\ C(2') - C(3') - C(4') \\ C(2') - C(3') - Br(1') \\ C(4') - C(3') - Br(1') \end{array}$	119(2) 113(2) 101(2) 104(2) 108(1) 107(1)
$\begin{array}{l} O(1') - C(1') - O(2') \\ O(2') - C(1') - C(2') \\ C(1') - C(2') - C(3') \\ C(2') - C(3') - C(4') \\ C(2') - C(3') - Br(1') \\ C(4') - C(3') - Br(1') \\ C(3') - C(4') - O(2') \end{array}$	119(2) 113(2) 101(2) 104(2) 108(1) 107(1) 104(1)
$\begin{array}{l} O(1') - C(1') - O(2') \\ O(2') - C(1') - C(2') \\ C(1') - C(2') - C(3') \\ C(2') - C(3') - C(4') \\ C(2') - C(3') - Br(1') \\ C(4') - C(3') - Br(1') \\ C(3') - C(4') - O(2') \end{array}$	119(2) 113(2) 101(2) 104(2) 108(1) 107(1) 104(1) 109(1)
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$\begin{array}{l} O(1') - C(1') - O(2') \\ O(2') - C(1') - C(2') \\ C(1') - C(2') - C(3') \\ C(2') - C(3') - C(4') \\ C(2') - C(3') - Br(1') \\ C(4') - C(3') - Br(1') \\ C(3') - C(4') - O(2') \\ C(4') - O(2') - C(1') \\ C(3') - C(4') - C(5') \\ O(2') - C(4') - O(3') \end{array}$	119(2) 113(2) 101(2) 104(2) 108(1) 107(1) 104(1) 109(1) 124(2) 105(1)
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$\begin{array}{c} O(1') - C(1') - O(2') \\ O(2') - C(1') - C(2') \\ C(1') - C(2') - C(3') \\ C(2') - C(3') - C(4') \\ C(2') - C(3') - Br(1') \\ C(4') - C(3') - Br(1') \\ C(3') - C(4') - O(2') \\ C(4') - O(2') - C(1') \\ C(3') - C(4') - C(5') \\ O(2') - C(4') - O(3') \\ C(5') - C(4') - O(3') \\ C(3') - C(4') - C(5') \\ C(3') - C(4') - C(5') \\ C(4') - C(5') - C(6') \\ C(5') - C(6') - C(7') \end{array}$	119(2) 113(2) 101(2) 104(2) 108(1) 107(1) 104(1) 109(1) 124(2) 105(1) 112(2) 105(2) 105(2)
$\begin{array}{c} O(1') - C(1') - O(2') \\ O(2') - C(1') - C(2') \\ C(1') - C(2') - C(3') \\ C(2') - C(3') - C(4') \\ C(2') - C(3') - Br(1') \\ C(4') - C(3') - Br(1') \\ C(3') - C(4') - O(2') \\ C(4') - O(2') - C(1') \\ C(3') - C(4') - C(5') \\ O(2') - C(4') - O(3') \\ C(5') - C(4') - O(3') \\ C(5') - C(4') - C(5') \\ O(3') - C(4') - C(5') \\ C(4') - C(5') - C(6') \\ C(6') - C(6') - C(7') \\ C(6') - C(6') - C(7') \\ C(6') - C(7') - O(3') \end{array}$	119(2) 113(2) 101(2) 104(2) 108(1) 107(1) 104(1) 109(1) 124(2) 105(1) 112(2) 105(2) 105(2) 106(2)
$\begin{array}{c} O(1') - C(1') - O(2') \\ O(2') - C(1') - C(2') \\ C(1') - C(2') - C(3') \\ C(2') - C(3') - C(4') \\ C(2') - C(3') - Br(1') \\ C(4') - C(3') - Br(1') \\ C(3') - C(4') - O(2') \\ C(4') - O(2') - C(1') \\ C(3') - C(4') - C(5') \\ O(2') - C(4') - O(3') \\ C(5') - C(4') - O(3') \\ C(5') - C(4') - C(5') \\ O(3') - C(4') - C(5') \\ C(4') - C(5') - C(6') \\ C(6') - C(6') - C(7') \\ C(6') - C(6') - C(7') \\ C(6') - C(7') - O(3') \end{array}$	119(2) 113(2) 101(2) 104(2) 108(1) 107(1) 104(1) 124(2) 105(1) 112(2) 105(2) 106(2) 106(2) 99(2) 111(2) 130(2)
$\begin{array}{l} O(1')-C(1')-O(2') \\ O(2')-C(1')-C(2') \\ C(1')-C(2')-C(3') \\ C(2')-C(3')-C(4') \\ C(2')-C(3')-Br(1') \\ C(4')-C(3')-Br(1') \\ C(3')-C(4')-O(2') \\ C(4')-O(2')-C(1') \\ C(3')-C(4')-O(3') \\ O(2')-C(4')-O(3') \\ O(2')-C(4')-O(3') \\ O(3')-C(4')-O(3') \\ O(3')-C(4')-C(5') \\ C(6')-C(6')-C(6') \\ C(6')-C(7')-C(6') \\ C(6')-C(7')-O(3') \\ O(4')-C(7')-O(3') \\ O(4')-C(7')-O(3') \end{array}$	119(2) 113(2) 101(2) 104(2) 108(1) 107(1) 104(1) 124(2) 105(1) 112(2) 105(2) 106(2) 106(2) 99(2) 111(2) 130(2)
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All the computations were carried out using the program system X-ray-63 compiled by Stewart.⁴

The results of the structure analysis show unequivocally that the bromine atom is placed in the β position. A multiparameter χ^2 -test ⁵ shows that there is no significant difference at the 95 % probability level between the two independent molecules in the asymmetric unit.

The molecule consists of two γ -lactone rings with one common atom (C(4)) (Fig. 1). These rings are not quite planar (Fig. 1), the standard deviations of the ring atoms from the best planes through them being 0.14 Å. The angles between the ring planes for each of the independent molecules are 89.0° and 88.7°, respectively.

The magnitudes of the standard deviations of the positional parameters of the lighter atoms do not permit a more detailed discussion of the structure.

Hydrogen atoms were not located.

The packing of the molecules in the crystal structure is mainly determined by van der Waals interactions. A short intermolecular distance of 3.15 Å. a value 0.2 Å smaller than that expected for a van der Waals contact, is found between the oxygen atom O(4') in one molecule and the bromine atom Br(1') in an adjacent molecule. This may perhaps be interpreted as evidence of a weak charge transfer bond. The corresponding angle C-Br. O is 160.9°.

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