

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 laboratory¹ 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°. 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 $0 \leq L \leq 6$ and hkl for $0 \leq k \leq 10$ using $\text{CuK}\alpha$ 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 positions	x/a	y/b	z/c
Br(1)	0.4372(2)	0.1574(2)	0.0266(3)
O(1)	0.5309(15)	-0.0651(13)	0.3340(20)
O(2)	0.6330(11)	0.0255(10)	0.2237(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)	0.3015(23)
C(2)	0.5094(23)	0.1086(21)	0.3350(31)
C(3)	0.5402(21)	0.1724(18)	0.2163(29)
C(4)	0.6463(17)	0.1238(17)	0.1905(23)
C(5)	0.6851(17)	0.1374(16)	0.0496(23)
C(6)	0.8022(21)	0.1393(20)	0.1043(29)
C(7)	0.8195(17)	0.1690(15)	0.2674(24)
Br(1')	0.1062(2)	0.0809(2)	0.1138(2)
O(1')	0.2852(15)	-0.1448(13)	0.3406(20)
O(2')	0.2592(11)	-0.0016(10)	0.4259(14)
O(3')	0.1369(12)	0.0395(11)	0.5614(16)
O(4')	0.1506(14)	0.1007(12)	0.7896(19)
C(1')	0.2224(15)	-0.0820(15)	0.3509(20)
C(2')	0.1091(19)	-0.0820(18)	0.2963(25)
C(3')	0.0849(16)	0.0242(14)	0.3015(20)
C(4')	0.1720(15)	0.0610(12)	0.4257(19)
C(5')	0.2059(18)	0.1606(16)	0.4420(24)
C(6')	0.2415(21)	0.1784(18)	0.6139(28)
C(7')	0.1723(17)	0.1082(15)	0.6685(22)

Thermal parameters

$$\text{Anisotropic } T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$$

	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Br(1)	60(2)	55(2)	119(4)	17(2)	-21(2)	-12(2)
Br(1')	67(2)	42(2)	48(3)	-16(1)	2(2)	8(2)

Isotropic $T = \exp[-B(\sin\theta/\lambda)^2]$

	B (e.s.d. $\times 10$)		B (e.s.d. $\times 10$)
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)	C(1')	1.1(3)
C(2)	3.5(5)	C(2')	2.2(4)
C(3)	2.5(5)	C(3')	1.2(3)
C(4)	1.7(4)	C(4')	0.9(3)
C(5)	1.8(4)	C(5')	1.7(4)
C(6)	3.1(5)	C(6')	2.8(5)
C(7)	1.6(4)	C(7')	1.7(4)

Table 2. Bond angles ($^{\circ}$). 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)
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)	106(2)
C(3)—C(4)—O(2)	104(2)
C(4)—O(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)	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)
C(5)—C(6)—C(7)	106(2)
C(6)—C(7)—O(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')—C(1')—C(2')	128(2)
O(1')—C(1')—O(2')	119(2)
O(2')—C(1')—C(2')	113(2)
C(1')—C(2')—C(3')	101(2)
C(2')—C(3')—C(4')	104(2)
C(2')—C(3')—Br(1')	108(1)
C(4')—C(3')—Br(1')	107(1)
C(3')—C(4')—O(2')	104(1)
C(4')—O(2')—C(1')	109(1)
C(3')—C(4')—C(5')	124(2)
O(2')—C(4')—O(3')	105(1)
C(5')—C(4')—O(2')	112(2)
C(3')—C(4')—O(3')	105(2)
O(3')—C(4')—C(5')	105(2)
C(4')—C(5')—C(6')	106(2)
C(5')—C(6')—C(7')	99(2)
C(6')—C(7')—O(3')	111(2)
C(6')—C(7')—O(4')	130(2)
O(4')—C(7')—O(3')	119(2)
C(7')—O(3')—C(4')	110(2)

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 -test⁵ 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.⁶ The corresponding angle C—Br···O is 160.9°.

Acknowledgement. I wish to thank Professor B. Jerslev, who suggested the problem and gave invaluable advice throughout the study, and lic. pharm. Birthe Jensen, who supervised the research.

REFERENCES

1. Hjeds, H. *Private communication*.
2. Hamilton, W. C., Rollett, J. S. and Sparks, R. A. *Acta Cryst.* **18** (1965) 129.
3. Cruickshank, D. W. J., Pilling, D. E., Bujosa, A., Lovell, F. M. and Truter, H. R. *Computing Methods in the Phase Problem*, Pergamon, Oxford 1961.
4. Stewart, J. M. Technical Report Tr 64—6, No. G-398, Computer Science Center of the University of Maryland, College Park 1964.
5. Hamilton, W. C. *Statistics in Physical Science*, New York 1964, Chap. 3—8.
6. Groth, P. and Hassel, O. *Acta Chem. Scand.* **16** (1962) 2311.

Received March 25, 1970.