

References

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The crystal structure consists of isolated 4,9-dibromo-1,6-dioxaspiro[4.4]nona-3,8-diene-2,7-dione molecules. The C—Br distances are 1.855 (10) and 1.837 (10) Å.

Comment

The preparation of 2-furanones has attracted considerable attention because these structures are present in many physiologically active substrates (Pattenden, 1978; Alonso, Orti, Branchadell, Oliva, Ortuno, Bertrán & Font, 1990). The chemistry of 2-furanones has been repeatedly reviewed (Rao, 1964, 1976). As part of a research program relating to the synthesis and structural study of pharmacologically interesting 2-furanone compounds, we have studied the synthesis and synthetic utilization of some derivatives of 1,4-pentadien-3-one-1,5-dicarboxylic acid (I). The bromination product of (I), 4-oxo-2,3,5,6-tetrabromopimelic acid, readily cyclizes upon heating to give the spiro-unsaturated lactone (II) in good yield.

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Structure of 4,9-Dibromo-1,6-dioxaspiro[4.4]nona-3,8-diene-2,7-dione,
C₇H₂Br₂O₄

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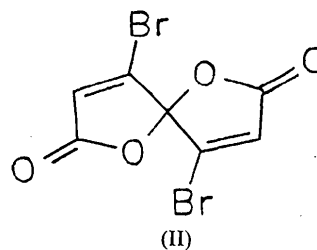
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Abstract

The molecule consists of two rings connected through a single C atom. The angle between the least-squares planes defined by the rings is 90.7 (4)°.



The unsaturated dibromospirolactone (II) has not been described previously and its structure could not be elucidated solely from spectroscopic data (IR, UV, ¹H and ¹³C NMR). The signals of the olefinic protons (singlet at 6.68 p.p.m.) and of the quaternary C atom (at 109.01 p.p.m. in ¹³C NMR spectra) are both very weak.

The X-ray diffraction study shows that the molecule consists of two spiro-fused unsaturated lactone rings which are planar within experimental error. The Br atoms lie in the spiro-lactone planes [O(1)—C(5)—C(4)—Br(1) = -176.3 (6), O(9)—C(5)—C(6)—Br(2) = -179.3 (7)°]. The double bonds adjacent to single bonds are enlarged and corresponding single bonds shortened (see Table 2). There is conjugation: C(4)—C(3)—C(2)=O(10) and C(6)=C(7)—C(8)=O(11), respectively. The crystal structure is in good agreement with the ¹H and ¹³C NMR spectra which indicate equivalence of corresponding atoms in the two rings.

The interesting structure and synthetic usefulness of (II) has led us to begin a systematic study of this fortuitous finding (Végh, Jakubcová, Kožíšek, Bencková & Dvorský, 1992).

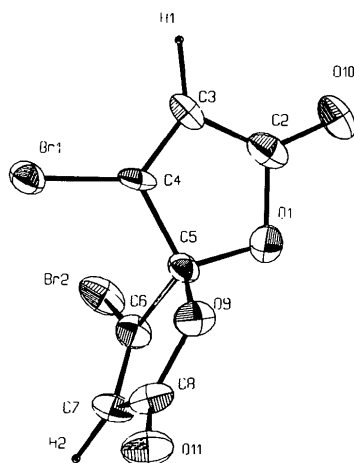


Fig. 1. The molecular structure (ORTEP; Johnson, 1971) of 4,9-dibromo-1,6-dioxaspiro[4.4]nona-3,8-diene-2,7-dione with atomic numbering scheme.

Experimental

Crystal data

$C_7H_2Br_2O_4$

$M_r = 309.90$

Monoclinic

$P2_1/a$

$a = 8.054 (3) \text{ \AA}$

$b = 16.013 (10) \text{ \AA}$

$c = 7.480 (3) \text{ \AA}$

$\beta = 111.28 (3)^\circ$

$V = 898.9 (8) \text{ \AA}^3$

$Z = 4$

$D_x = 2.290 \text{ Mg m}^{-3}$

$D_m = 2.23 (2) \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation

$\lambda = 1.54178 \text{ \AA}$

Cell parameters from 12 reflections

$\theta = 16-32^\circ$

$\mu = 11.4 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Plate

$0.60 \times 0.20 \times 0.15 \text{ mm}$

Data collection

Syntex $P2_1$ diffractometer

$\theta-2\theta$ scans

Absorption correction:

empirical

$T_{\min} = 0.352$, $T_{\max} =$

0.951

1699 measured reflections

1498 independent reflections

1683 observed reflections

$[F_o > 5\sigma(F)]$

$R_{\text{int}} = 0.143$

$\theta_{\max} = 64^\circ$

$h = -9 \rightarrow 8$

$k = 0 \rightarrow 18$

$l = 0 \rightarrow 8$

3 standard reflections

monitored every 97

reflections

intensity variation: 2.4%

Refinement

Refinement on F

Final $R = 0.0525$

$wR = 0.0623$

$S = 2.3$

1287 reflections

118 parameters

H-atom parameters not refined

Unit weights applied

$(\Delta/\sigma)_{\max} = 0.010$

$\Delta\rho_{\max} = 0.33 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.26 \text{ e \AA}^{-3}$

Atomic scattering factors

from *SHELX76* for C, H

and O, and *International*

Tables for X-ray Crystallography (1974, Vol. IV)

for Br atoms

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Br(1)	0.3127 (1)	0.1331 (1)	0.0780 (2)	50
Br(2)	0.1380 (2)	0.2303 (1)	0.5094 (2)	59
O(1)	-0.1211 (9)	0.0887 (5)	0.2191 (11)	54 (3)
C(2)	-0.2013 (16)	0.1312 (7)	0.0482 (17)	56 (5)
C(3)	-0.0634 (14)	0.1559 (7)	-0.0227 (17)	55 (5)
C(4)	0.0881 (13)	0.1288 (6)	0.0933 (12)	34 (3)
C(5)	0.0646 (13)	0.0845 (6)	0.2600 (14)	40 (4)
C(6)	0.1700 (13)	0.1208 (6)	0.4561 (13)	39 (4)
C(7)	0.2802 (15)	0.0626 (7)	0.5585 (16)	51 (5)
C(8)	0.2545 (16)	-0.0134 (7)	0.4463 (16)	52 (5)
O(9)	0.1202 (10)	0.0011 (4)	0.2708 (10)	50 (3)
O(10)	-0.3593 (10)	0.1413 (7)	-0.0123 (15)	89 (5)
O(11)	0.3304 (13)	-0.0777 (5)	0.4786 (13)	76 (4)

Table 2. Geometric parameters (\AA , $^\circ$)

Br(1)—C(4)	1.855 (10)	C(4)—C(5)	1.505 (15)
Br(2)—C(6)	1.837 (10)	C(5)—C(6)	1.519 (13)
O(1)—C(2)	1.384 (13)	C(5)—O(9)	1.402 (12)
O(1)—C(5)	1.415 (13)	C(6)—C(7)	1.323 (14)
C(2)—C(3)	1.449 (20)	C(7)—C(8)	1.450 (16)
C(2)—O(10)	1.197 (14)	C(8)—O(9)	1.384 (12)
C(3)—C(4)	1.289 (13)	C(8)—O(11)	1.177 (14)
C(2)—O(1)—C(5)	109.0 (9)	O(1)—C(5)—O(9)	110.4 (9)
O(1)—C(2)—O(10)	119.4 (11)	O(1)—C(5)—C(6)	111.5 (9)
O(1)—C(2)—C(3)	108.0 (10)	C(6)—C(5)—O(9)	104.7 (8)
C(3)—C(2)—O(10)	132.5 (12)	Br(2)—C(6)—C(5)	120.1 (7)
C(2)—C(3)—C(4)	109.0 (10)	C(5)—C(6)—C(7)	108.2 (9)
Br(1)—C(4)—C(3)	130.7 (8)	Br(2)—C(6)—C(7)	131.6 (8)
C(3)—C(4)—C(5)	110.1 (10)	C(6)—C(7)—C(8)	109.4 (10)
Br(1)—C(4)—C(5)	119.2 (7)	C(7)—C(8)—O(11)	131.4 (11)
O(1)—C(5)—C(4)	103.9 (8)	C(7)—C(8)—O(9)	107.8 (9)
C(4)—C(5)—O(9)	111.3 (8)	O(9)—C(8)—O(11)	120.7 (10)
C(4)—C(5)—C(6)	115.2 (8)	C(5)—O(9)—C(8)	109.7 (8)

Colourless crystals of poor quality were obtained by slow crystallization from *n*-hexane. Experimental density was measured by flotation (CHBr_3 , C_6H_6). The merging factor ($R_{\text{int}} = 0.194$ for 238 reflections) was high, so some systematically absent reflections were examined by ψ scan. However, the space group $P2_1/a$ was confirmed and the high R_{int} was considered to result from absorption as well as the strong Renninger effect. Empirical correction for absorption was applied using *DIFABS* (Walker & Stuart, 1983) after isotropic refinement. The structure was solved by the Patterson method (Sheldrick, 1990) and refined by full-matrix least-squares technique (Sheldrick, 1976). H atoms were placed in idealized positions ($\text{C—H} = 1.08 \text{ \AA}$) with isotropic thermal parameters $U_{\text{iso}} = 0.090 \text{ \AA}^2$. All calculations were carried out on the CDC-4680 computer system. *PARST* was used for geometrical calculations (Nardelli, 1983).

Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55791 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1003]

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p-Bromobenzoate Derivative of 3-(*tert*-Butyldimethylsilyl)-5-hydroxy-2(5*H*)-furanone

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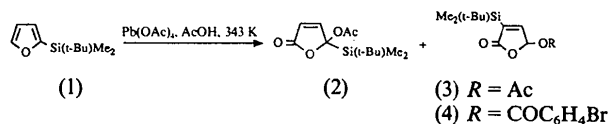
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Abstract

In 3-(*tert*-butyldimethylsilyl)-2-oxo-5*H*-5-furyl 4-bromobenzoate, the furan ring is almost planar with a maximum deviation of 0.047 (6) Å, while the benzene ring is essentially planar [maximum deviation 0.012 (5) Å]; the best mean planes of the two rings are inclined at an angle of 73.7°. The average bond distances are: Si—C 1.865 (7), C_{sp³}—C_{sp³} 1.523 (9), C_{sp²}—C_{sp²} 1.487 (7), C—C_{arom} 1.381 (7), C_{sp³}—O 1.423 (6), C_{sp²}—O 1.362 (6) and C=O 1.204 (6) Å.

Comment

Treatment of 2-(*tert*-butyldimethylsilyl)furan (1) with lead tetraacetate in acetic acid at 343 K for 2 h provided compounds (2) and (3) in a 2:1 ratio. The



major compound (2) was identified as 5-(*tert*-butyldimethylsilyl)-5-acetoxy-2(5*H*)-furanone by NMR, IR and MS spectra. The minor compound was identified by converting the acetate of compound (3) into a *p*-bromobenzoate (4) and performing an X-ray structure determination. The structure consists of discrete molecules separated by normal van der Waals distances.

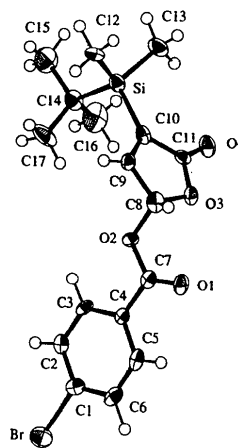


Fig. 1. ORTEP (Johnson, 1976) drawing of the title compound showing the labelling of the non-H atoms. Thermal ellipsoids are shown at 50% probability levels; H atoms are assigned arbitrary radii.

Experimental

Crystal data

C₁₇H₂₁BrO₄Si
M_r = 397.34
 Triclinic
P $\bar{1}$
a = 7.350 (4) Å
b = 19.906 (10) Å
c = 6.726 (5) Å
 α = 93.93 (6)°
 β = 109.10 (6)°
 γ = 87.59 (5)°
V = 927 (1) Å³
Z = 2

D_x = 1.423 Mg m⁻³
 Mo *K*α radiation
 λ = 0.71069 Å
 Cell parameters from 25 reflections
 θ = 10–15°
 μ = 2.27 mm⁻¹
T = 152 (1) K
 Block
 0.50 × 0.40 × 0.30 mm
 Colourless

Data collection

Rigaku AFC-6S diffractometer
 $\omega/2\theta$ scans, width (1.78 + 0.35tan θ)°, rate 8.0° min⁻¹ in ω
 Absorption correction: empirical (North, Phillips & Mathews, 1968)
T_{min} = 0.723, *T_{max}* = 0.999
 3560 measured reflections

3279 independent reflections
 2289 observed reflections
 $[I > 3\sigma(I)]$
R_{int} = 0.0255
 θ_{max} = 25°
h = 0 → 8
k = -23 → 23
l = -7 → 7
 3 standard reflections
 frequency: 100 min
 intensity variation: <0.7%

Refinement

Refinement on *F*
 Final *R* = 0.048
 wR = 0.033
S = 3.49
 2279 reflections
 271 parameters

Only coordinates of H atoms refined
 $w = 1/(\sigma^2 F)$
 $(\Delta/\sigma)_{\text{max}}$ = 0.05
 $\Delta\rho_{\text{max}}$ = 0.68 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.71 e Å⁻³