Conformational Study of 6-*p*-Bromophenyl-1,4-oxathian-2-one

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The crystal structure of the title compound was determined by *X*-ray diffraction. The crystals have monoclinic symmetry with $a = 7.129(4)$, $b = 8.698(6)$, $c = 16.633(4)$ Å, $\beta = 97.13(6)°$, and space group $P2_1/c$. For 2 001 observed independent reflections collected with a four-circle diffractometer the *R*-factor reached 0.042 after block-diagonal least-squares refinement. The conformation of the lactone ring is a perfect boat with a planar ester group. The aromatic ring is nearly perpendicular to the bottom of the boat. The conformation of the lactone in solution is discussed in relation to the solid-state structure and on the basis of n.m.r. and dipole measurements.

In δ-lactones the planar ester moiety[1] allows the six-membered ring two distinct conformations: half-chair and boat.[2–9] Both of these are known to occur in the solid state.[10–12] In solution six-membered lactones are generally believed to prefer the half-chair.[5] A recent microwave study of δ-valerolactone revealed two different forms in the gas phase, with an energy difference of 2.5 kJ mol^{-1} in favour of the half-chair.[9] These experimental data were backed by force-field calculations. Thus it seems that in absence of strong steric interactions, valerolactones prefer the half-chair conformation. Kelstrup suggested that 6-methyl-1,4-oxathian-2-one, an analogue of valerolactone, exists as a rapidly equilibrating mixture of the two conformers.[13] A ^{1}H n.m.r. study of 1,4-oxathian-2-ones by one of us arrived at the conclusion that oxathianones probably adopt the boat conformation.[14] The present paper describes the crystal structure determination of 6-*p*-bromophenyl-1,4-oxathian-2-one.

Bond lengths, bond angles, and torsion angles of the oxathianone are listed in Tables 3—5. The lactone ring assumes a classical boat conformation, the bottom of the boat [O(1),C(2),S(4),C(5)] being almost planar (maximum deviation 0.019 Å). The sides of the boat are also planar, as can be seen from the torsion angles C(6)–O(1)–C(2)–C(3) 1.3° and C(3)–S(4)–C(5)–C(6) 1.7°. Other torsion angles indicate a normal cyclohexane-like arrangement. The ring is, however, flattened in comparison with 1,4-oxathiane. The phenyl substituent bisects the boat but is slightly twisted out of the perpendicular plane towards C(5), apparently to avoid close contact between the *ortho* and the axial hydrogen atoms. The angle between the least-squares planes of the boat bottom and the phenyl ring is 72.2°. The interatomic distance between the axial hydrogen atoms at the bow and the stern [2.49(5) Å] is greater than the van der Waals range. Bond lengths and angles are normal.

To our knowledge this is the first time a non-hindered δ-lactone has been shown to prefer the boat conformation. The *p*-bromophenyl substituent would seem to be as comfortable with either possible conformation. Besides crystal packing forces, the reason for the unusual conformation appears to be that the oxathianone lacks the unfavourable eclipsed C–H interaction of the boat δ-valerolactone. If the eclipsed C–H interactions contribute 4 kJ mol^{-1} per pair, the conformational energy for oxathianone may be calculated to be $-2.5 + 2 \times 4 = 5.5$ kJ mol^{-1} in favour of the boat form.

The question of the prevalent solution conformation of oxathianone was then investigated by several methods. The i.r. carbonyl frequency of δ-lactones has been correlated with the ring conformation.[2,5,7] Unfortunately, these results cannot be applied to oxathianones.[14] Equally inconclusive results are obtained from proton n.m.r. spectroscopy. Analysis of the spectrum gives the following vicinal coupling constants between the protons at C(5) and C(6): δ(C_6D_6) J_{ae} 2.75, J_{aa} 11.6; δ($CDCl_3$) J_{ae} 3.5 and J_{aa} 10.6 Hz.† These are perfectly compatible with the structure obtained by *X*-ray diffraction but are also compatible with the half-chair form or an equilibrating mixture of the two.

The ^{13}C n.m.r. spectrum of the lactone exhibits four signals for the ring carbon atoms and four aromatic carbon signals which are easily assigned on the basis of the chemical shifts alone (Table 6). The spectra recorded for solutions in C_6D_6, $CDCl_3$, and $(CD_3)_2SO$ and in the solid state are quite similar, the largest variation being observed in the carbonyl shift (1.7 p.p.m.). The differences are probably solvent-induced rather than due to any structural change. The signals for the aromatic carbons are broadened and overlapping at the spinning rate used in acquiring the solid-state spectrum. On the assumption that the boat and the half-chair have markedly different carbon spectra, these results strongly suggest that the lactone has the same conformation in the three solvents and in the solid state (the boat). Chemical shifts in the solid state and in solution usually coincide unless there are some specific perturbing effects.[15–19] Similarly, lack of dependence of the chemical shifts on the dielectric constant of the medium (benzene ε 2.3, Me_2SO ε 46.7) argues against the possibility of a conformational equilibrium; the position of such an equilibrium would be expected to vary according to the polarity of the medium since the two conformers have different dipole moments (see later).

Dipole moments are often very useful in the study of conformations when the conformers in question have unequal dipoles. A dipole moment of 3.73 D may be calculated for the boat form of the title compound, from the *X*-ray geometry and the following bond moments: C=O 3.55, C–O (conj.) 0.55, C–O 0.95, C–S 1.12, C–Br 1.57 D. The dipole moment for the hypothetical half-chair form (2.98 D) was calculated on the basis of a molecular geometry similar to that of the half-chair valerolactone.[9] The dipole moment of 3.50 ± 0.15 D was obtained for the title compound in benzene by the dilute solution approach, using the Guggenheim–Smith method[20] of calculation. This dipole moment implies that the lactone in benzene is more likely to have a boat than a half-chair form. However, the simple bond moment scheme employed in calculation of the model dipoles may not be very accurate in this case, since it does not take into account induced dipoles.[9]

On the whole, the foregoing results support the existence of the boat form in solution, though the half-chair cannot be

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† The difference in the coupling constants in $CDCl_3$ and C_6D_6 may be due to the large uncertainty of the chloroform values resulting from the poor resolution of the ABX pattern.

Table 1. Fractional atomic co-ordinates (× 10^4) for the non-hydrogen atoms (× 10^5 for Br and S) and the equivalent isotropic thermal parameters (× 10^3)

$$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	U_{eq}/Å^2
Br	−59 047(6)	44 937(5)	33 382(3)	62
S(4)	14 987(15)	15 847(12)	1 827(6)	54
O(1)	1 090(3)	4 573(2)	1 122(1)	37
O(2)	2 965(4)	5 644(3)	343(1)	48
C(2)	2 478(5)	4 497(4)	646(2)	36
C(3)	3 331(5)	2 940(4)	547(2)	43
C(5)	−152(4)	1 985(4)	896(2)	42
C(6)	553(4)	3 185(4)	1 515(2)	35
C(7)	−964(4)	3 624(3)	2 025(2)	32
C(8)	−957(5)	2 968(3)	2 778(2)	40
C(9)	−2 413(4)	3 254(3)	3 238(2)	42
C(10)	−3 857(4)	4 193(3)	2 936(1)	36
C(11)	−3 863(4)	4 898(4)	2 196(2)	43
C(12)	−2 418(4)	4 590(4)	1 742(1)	41

Table 2. Fractional atomic co-ordinates (× 10^3), isotropic thermal parameters (× 10^3), and bond distances (Å) for the hydrogen atoms

	x	y	z	U_{iso}/Å^2	Bond length
H1[C(3)]	409(4)	249(3)	106(2)	49(10)	1.02(3)
H2[C(3)]	414(5)	299(4)	17(2)	64(13)	0.91(4)
H1[C(5)]	−21(6)	116(5)	119(2)	81(13)	0.87(4)
H2[C(5)]	−128(4)	221(3)	62(2)	42(9)	0.90(3)
H[C(6)]	182(4)	280(3)	188(2)	33(8)	1.07(3)
H[C(8)]	2(5)	233(4)	304(2)	47(10)	0.95(3)
H[C(9)]	−244(5)	278(4)	372(2)	50(10)	0.90(3)
H[C(11)]	−493(5)	555(3)	200(2)	50(10)	0.97(3)
H[C(12)]	−243(4)	498(3)	126(2)	34(8)	0.87(3)

Table 3. Bond distances for non-hydrogen atoms with standard deviations in parentheses

Bond	Distance (Å)	Bond	Distance (Å)
C(1)–O(1)	1.344(4)	C(7)–C(8)	1.372(5)
C(2)–O(2)	1.188(4)	C(7)–C(12)	1.372(5)
C(2)–C(3)	1.502(5)	C(8)–C(9)	1.387(5)
C(3)–S(4)	1.808(4)	C(9)–C(10)	1.361(5)
C(5)–S(4)	1.805(4)	C(10)–Br	1.888(4)
C(5)–C(6)	1.508(5)	C(10)–C(11)	1.375(5)
C(6)–O(1)	1.447(4)	C(11)–C(12)	1.377(5)
C(6)–C(7)	1.504(5)		

excluded with certainty merely on the basis of i.r., n.m.r., and dipole moment evidence.

Experimental

Crystal Data.—$C_{10}H_9BrO_2S$, $M = 273.15$, monoclinic, $a = 7.129(4)$, $b = 8.698(6)$, $c = 16.633(14)$ Å, $\beta = 97.13(6)°$, $V = 1\,023$ Å^3 (by least-squares refinement on diffractometer angles for 24 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P2_1/c$ (No. 14), $Z = 4$, $D_m = 1.77$, $D_c = 1.77$ g cm^{-3}. Colourless, prismatic crystals.[21] Approximate crystal dimensions 0.2 × 0.3 × 0.6 mm, μ(Mo-K_α) = 44.2 cm^{-1}.

Data Collection and Processing.—Nicolet P3 diffractometer, $\theta/2\theta$ mode with θ scan width = 1.0, θ scan speed 2.0—30.0 °/min^{-1}, graphite-monochromated Mo-K_α radiation; 3 219 reflections measured ($1.5 \leqslant \theta \leqslant 30.5°$, $+h,k,l$), 3 002 unique (empirical absorption correction ψ-scan data), giving 2 001 with $I > 3\sigma(I)$.

Table 4. Bond angles for non-hydrogen atoms with standard deviations in parentheses

Bond	Angle (°)	Bond	Angle (°)
C(6)–O(1)–C(2)	118.7(2)	C(6)–C(7)–C(8)	119.1(3)
O(1)–C(2)–O(2)	118.9(3)	C(6)–C(7)–C(12)	121.8(3)
O(1)–C(2)–C(3)	116.5(3)	C(8)–C(7)–C(12)	119.0(3)
O(2)–C(2)–C(3)	124.5(3)	C(7)–C(8)–C(9)	120.7(3)
C(2)–C(3)–S(4)	109.8(2)	C(8)–C(9)–C(10)	119.2(3)
C(3)–S(4)–C(5)	99.0(2)	C(9)–C(10)–Br	119.1(3)
S(4)–C(5)–C(6)	113.2(2)	C(9)–C(10)–C(11)	121.1(3)
C(5)–C(6)–O(1)	110.7(3)	Br–C(10)–C(11)	119.8(3)
C(5)–C(6)–C(7)	111.1(3)	C(10)–C(11)–C(12)	119.0(3)
O(1)–C(6)–C(7)	107.0(3)	C(11)–C(12)–C(7)	121.0(3)

Table 5. Selected torsion angles; estimated standard deviations in parentheses

Bond	Torsion angle (°)
O(1)–C(6)–C(7)–C(12)	43.6(4)
O(1)–C(6)–C(7)–C(8)	−140.4(3)
O(1)–C(2)–C(3)–S(4)	55.6(3)
C(2)–C(3)–S(4)–C(5)	−49.4(3)
C(3)–S(4)–C(5)–C(6)	−1.7(3)
S(4)–C(5)–C(6)–O(1)	54.0(3)
S(4)–C(5)–C(6)–C(7)	172.7(2)
C(5)–C(6)–O(1)–C(2)	−60.8(3)
C(5)–C(6)–C(7)–C(8)	98.7(3)
C(5)–C(6)–C(7)–C(12)	−77.3(4)
C(6)–O(1)–C(2)–O(2)	−177.6(3)
C(6)–O(1)–C(2)–C(3)	1.3(4)

Table 6. ^{13}C N.m.r. shifts of 6-*p*-bromophenyl-1,4-oxathian-2-one

Carbon atom	C_6D_6	$CDCl_3$	$(CD_3)_2SO$	Solid
5	25.85	26.06	25.33	26.09
3	31.24	31.61	30.30	32.81
6	79.02	79.68	77.99	78.54
para[a]	122.95	123.12	121.83	
ortho	128.50	127.66	128.50	
meta	131.96	132.04	131.41	131.42[b]
ipso	137.20	136.49	137.21	138.73[b]
2	166.03	167.22	168.18	169.70

[a] Aromatic carbon atoms were tentatively assigned on the basis of known substituent shift parameters.[15] [b] The aromatic carbon atoms gave only two broad signals.

Structure Analysis and Refinement.—Direct methods (all atoms). Block-diagonal least squares refinement with all non-hydrogen atoms anisotropic and with all hydrogen atoms isotropic. The weighting scheme $w = 1/\sigma^2(F_o)$, with $\sigma(F_o)$ from counting statistics, gave satisfactory agreement analysis. Final R and R_w values are 0.042 and 0.040. Programs and computers used and sources of scattering factors are given in ref. 22. The molecule and its numbering scheme are presented in the Figure. The co-ordinates and non-hydrogen equivalent isotropic temperature factors are listed in Table 1. Co-ordinates and isotropic temperature factors for hydrogen atoms are given in Table 2.

Dipole Moment Determination.—The dipole moment was determined by measuring the dielectric constants (Dipolmäter DM01) and refractive indices of dilute solutions of the lactone in

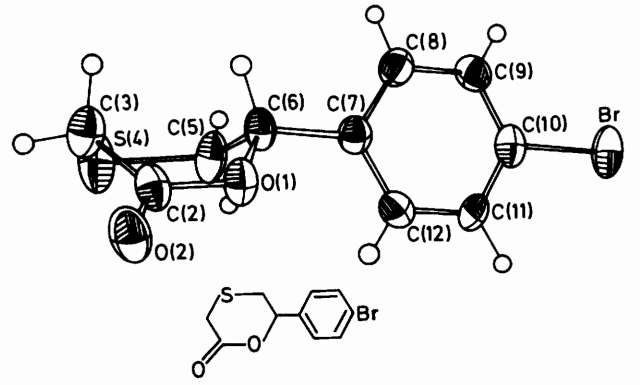

Figure. ORTEP Drawing of 6-*p*-bromophenyl-1,4-oxathian-2-one with the atoms represented by their 50% probability ellipsoids for thermal motion

benzene at 25.0 °C. The slopes $d\varepsilon/dw$ and dn/dw (w = weight fraction of solute) were used to calculate the dipole moments according to the Guggenheim–Smith method:[20] 3.50 ± 0.13 D. The dipole meter and the refractometer were calibrated with pure solvents. The solid-state ^{13}C n.m.r. spectrum was obtained by magic angle spinning, cross polarization, and high-power decoupling techniques with a JEOL JMN-FX-200 spectrometer. The powdered sample was packed in a rotor made of KelF. The spinning speed was 3 200—3 500 rev. min^{-1}. The chemical shifts were determined against hexamethylbenzene standard set at 132.300 p.p.m. The cross polarization contact time was 5 ms and the recycle time 10 s.

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References

1 R. Huisgen and H. Ott, *Tetrahedron*, 1959, **6**, 253.
2 K. K. Cheung, K. H. Overton, and G. A. Sim, *Chem. Commun.*, 1965, 634.
3 N. L. Allinger and S. H. M. Chang, *Tetrahedron*, 1977, **33**, 1561.
4 P. Äyräs and K. Pihlaja, *Tetrahedron*, 1973, **29**, 1311.
5 F. I. Carroll, G. N. Mitchell, J. T. Blackwell, A. Sobti, and R. Meck, *J. Org. Chem.*, 1974, **39**, 3890.
6 R. N. Johnson and N. V. Riggs, *Tetrahedron Lett.*, 1967, 5119.
7 F. I. Carroll and J. T. Blackwell, *Tetrahedron Lett.*, 1970, 4173.
8 A. McL. Mathieson, *Tetrahedron Lett.*, 1963, 81.
9 T. Philip, R. L. Cook, T. B. Malloy, Jr., N. L. Allinger, S. Chang, and Y. Yuh, *J. Am. Chem. Soc.*, 1981, **103**, 2151.
10 S. Axiotis, J. Dreux, M. Perrin, and J. Royer, *Tetrahedron*, 1982, **38**, 499.
11 G. Kartha and D. J. Haas, *J. Am. Chem. Soc.*, 1964, **86**, 3630.
12 H. Ferres, I. K. Hatton, L. J. A. Jennings, A. W. R. Tyrrell, and D. J. Williams, *Tetrahedron Lett.*, 1983, **24**, 3769.
13 E. Kelstrup, *J. Chem. Soc., Perkin Trans. 1*, 1979, 1029.
14 J. K. Koskimies, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1449.
15 E. Pretsch, T. Clerc, J. Seibl, W. Simon, 'Tabellen zur Strukturaufklärung organischer Verbindugen mit spektroskopischen Methoden,' Springer Verlag, Berlin-Heidelberg, 1981, p. C120.
16 E. T. Lippmaa, M. A. Alla, T. J. Pehk, and G. Engelhardt, *J. Am. Chem. Soc.*, 1978, **100**, 1929.
17 D. L. Van der Hart, W. L. Earl, and A. N. Garroway, *J. Magn. Reson.*, 1981, **44**, 361.
18 G. R. Hayes, *Analyst (London)*, 1982, **107**, 241.
19 Ching-jer Chang, L. E. Diaz, W. R. Woolfenden, and D. M. Grant, *J. Org. Chem.*, 1982, **47**, 5318.
20 O. Exner, 'Dipole Moments in Organic Chemistry,' Georg Thieme, Stuttgart, 1975, p. 14; see also O. Exner, *Collect Czech. Chem. Commun.*, 1981, **46**, 1002.
21 J. Koskimies, *Acta Chem. Scand., Ser. B*, 1984, **38**, 101.
22 J. Korvenranta, H. Saarinen, and M. Näsäkkälä, *Inorg. Chem.*, 1982, **21**, 4296.

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