The Molecular Structures of Five- and Six-membered Cyclic Sulphonates

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RECENT studies in the hydrolysis of sulphur- and phosphorus-containing cyclic esters have endeavoured to relate the rates of hydrolysis with molecular structure.[1,2] The five-membered sultone, *o*-hydroxy-α-toluenesulphonic acid (I), is hydrolyzed 10^4 times faster than the six-membered sultone, 2-*o*-hydroxyphenylethanesulphonic acid (II).[2] We have determined the molecular structures of (I) and (II) by *X*-ray diffraction.

The five-membered sultone (I) crystallized out with the space group, *Pbca*, with cell constants of $a = 5{\cdot}66$, $b = 16{\cdot}06$, $c = 16{\cdot}12$ Å and $Z = 8$. The six-member sultone had a space group of $P2_1/a$ with cell constants $a = 11{\cdot}12$, $b = 8{\cdot}77$, $c = 9{\cdot}67$ Å, $\gamma = 111{\cdot}8°$, and $Z = 4$. Both these structures were solved by MAGIC,[3] a computer program that uses the direct method for solving the phase problem.[4] For (I), the final *R* factor is 0·093 for 437 reflections, and for (II) it is 0·090 for 373 reflections.

The molecular configurations of the sultones (I) and (II) are shown in Figures 1 and 2. Table 1 gives a list of bond distances and Table 2 bond angles for the two cyclic ester structures. The bond distances for the two structures show similar bond lengths for similar types of bonds. On the other hand the angles suggest that there is a considerable amount of strain in the five-membered sultone as compared to the six-membered one. The C(7)–S–O(3) angle (96·1) is 5·3° smaller than

TABLE 1

Bond distances in five- and six-membered sultones

	Five-membered ring (I)		Six-membered ring (II)	
Bond	Length (Å)	e.s.d.	Length (Å)	e.s.d.
S–O(1)	1·411	0·008	1·412	0·015
S–O(2)	1·421	0·008	1·444	0·010
S–O(3)	1·627	0·008	1·594	0·009
S–C(8)	—	—	1·747	0·014
S–C(7)	1·791	0·011	—	—
O(3)–C(1)	1·413	0·012	1·435	0·020
C(1)–C(2)	1·387	0·013	1·411	0·019
C(2)–C(3)	1·367	0·015	1·414	0·022
C(3)–C(4)	1·394	0·016	1·388	0·021
C(4)–C(5)	1·372	0·015	1·369	0·019
C(5)–C(6)	1·371	0·014	1·421	0·022
C(6)–C(1)	1·363	0·014	1·366	0·019
C(6)–C(7)	1·541	0·015	1·516	0·020
C(7)–C(8)	—	—	1·527	0·021

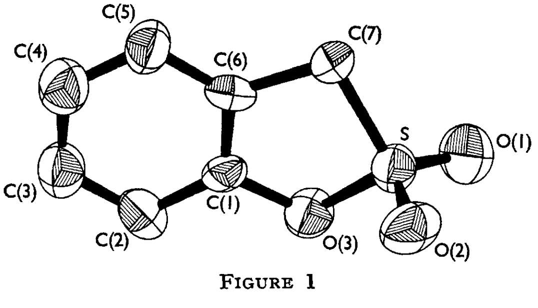

FIGURE 1

the C(8)–S–O(3) (101·4°) and the S–O(3)–C(1) for 5-membered compound is 108·9° compared to 116·9° for the same angle in the six-membered ring (a difference of 8·0°). The strain introduced in the five-membered ring as demonstrated by the difference in angles may be the basis for the difference in the rates of hydrolysis of the two compounds.[5]

TABLE 2

Bond angles in (I) and (II)

Angle	(I)	(II)
O(1)–S–O(3)	118·9°*	117·2°*
O(1)–S–O(3)	106·8	105·3
O(2)–S–O(3)	107·7	110·1
C(8,7)–S–O(1)	114·2	111·7
C(8,7)–S–O(2)	110·2	109·8
C(8,7)–S–O(3)	96·1	101·4
S–O(3)–C(1)	108·9	116·9
O(3)–C(1)–C(2)	120·5	111·8
C(1)–C(2)–C(3)	116·2	114·0
C(2)–C(3)–C(4)	119·8	120·2
C(3)–C(4)–C(5)	122·7	121·7
C(4)–C(5)–C(6)	117·8	121·6
C(5)–C(6)–C(1)	119·0	114·1
C(6)–C(1)–C(2)	124·5	127·9
C(6)–C(7)–C(8)	—	113·3
O(3)–C(1)–C(6)	115·0	120·3
C(1)–C(6)–C(7)	112·6	126·1
C(6,7)–C(7,8)–S	101·4	108·7

* Average e.s.d. about 1°.

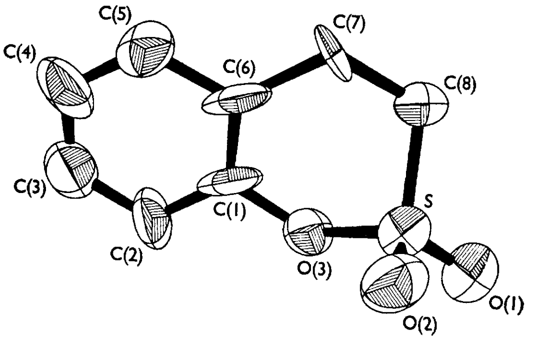

FIGURE 2

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[1] T. Beineke, *Chem. Comm.*, 1966, 860; O. R. Zaborsky and E. T. Kaiser, *J. Amer. Chem. Soc.*, 1966, **88**, 3084; J. Kumamoto, J. R. Cox, Jr., and F. H. Westheimer, *ibid.*, 1956, **78**, 4858; T. A. Steitz and W. N. Lipscomb, *ibid.*, 1965, **87**, 2488.

[2] E. T. Kaiser, I. R. Katz, and T. F. Wulfer, *J. Amer. Chem. Soc.*, 1965, **87**, 3781; E. T. Kaiser, K. Kudo, and O. R. Zaborsky, *ibid.*, in the press.

[3] A. Stone, R. Dewar, and E. Fleischer, to be published.

[4] D. Sayre, *Acta Cryst.*, 1952, **5**, 60; I. L. Karle, K. S. Dragonette, and S. A. Brenner, *ibid.*, 1965, **19**, 713.

[5] Evidence has been obtained that the hydrolyses of the five-membered cyclic phosphorus-containing esters proceed by way of trigonal bipyramid intermediates in which the ring is constrained to span one apical and one equatorial position. *Cf.*, P. C. Haake and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1961, **83**, 1102 and E. A. Dennis and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1966, **88**, 3432. Experiments are now in progress (O. R. Zaborsky, unpublished work) to determine the presence or absence of similar intermediates in hydrolyses of sulphur-containing esters.