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The Molecular Structure in the Solid State of a Dimerisation Product of Benzo[*c*]thiopyrylium-4-oxide

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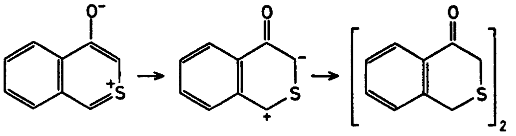
The major product of the dimerisation $2C_9H_8OS \rightarrow (C_9H_6OS)_2$ belongs to the orthorhombic system with space group *Fdd*2 and cell dimensions $a = 7.722(2)$ Å, $b = 21.991(4)$ Å, $c = 17.267(5)$ Å. The unit cell contains eight molecules with two-fold axes of symmetry. The structure was solved by the heavy atom method and refined by full-matrix least squares technique to an R-value of 4.4 % ($R_w = 4.7$ %) for 1003 reflections recorded on an automatic four circle diffractometer. The isomer has the *syn* structure. One of the intramolecular C–C distances between overlying benzene rings is as short as 3.242(6) Å, and the C–C bridge bond is 1.577(5) Å, which is significantly longer than a normal C–C single bond.

Dimerisation of thiopyrylium-4-oxides are studied by Undheim *et al.*[1] by spectroscopic methods. For benzo[c]thiopyrylium-4-oxide the reaction scheme is:



The product consists of two isomeric dimers. Weak indications from NMR- and UV-studies suggest that the major isomer has a *syn* structure (see Fig. 1). In order to settle the structural problem an X-ray crystallographic investigation has been carried out.

The crystals are orthorhombic with space group *Fdd*2, cell dimensions $a = 7.722(2)$ Å, $b = 21.991(4)$ Å, $c = 17.267(5)$ Å, and eight molecules in the unit cell. With 2θ-max = 60° and Mo$K\alpha$-radiation (graphite crystal monochromator), 1225 reflections were measured on an automatic four-circle diffractometer. With an observed-unobserved cutoff at $2.5\sigma(I)$, 1003 were recorded as observed. No corrections for absorption (crystal size 0.2 mm × 0.2 mm × 0.3 mm) or secondary extinction effects have been carried out.

The structure was solved by the heavy atom method and refined by full-matrix least squares technique.[2],* Anisotropic temperature factors were introduced for all non-hydrogens. Weights in least squares were obtained from the standard deviations in intensities, $\sigma(I)$, taken as where

$$\sigma(I) = [C_T + (0.02C_N)^2]^{\frac{1}{2}}$$

C_T is the total number of counts, and C_N the net count (peak minus background). The atomic form factors were those of Hanson *et al.*[3] except for hydrogen.[4] The R-value arrived at was 4.4 %

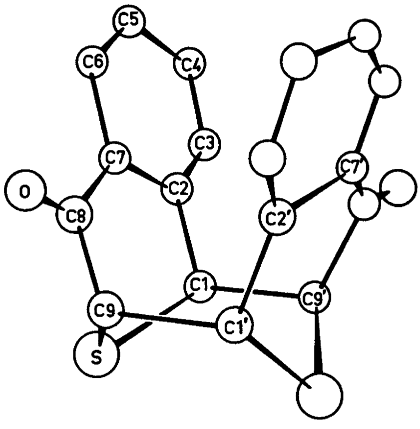


Fig. 1. Schematical drawing of the molecule.

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* All programs used are included in this reference.

Table 1. Final fractional coordinates and anisotropic thermal vibration parameters with estimated standard deviations (multiplied by 10^5 for non-hydrogens and 10^4 for hydrogen atoms). H*n* is bonded to C*n*.

ATOM	X	Y	Z	B	B11	B22	B33	B12	B13	B23
S	5489(13)	24589(4)	24970		1832(18)	164(2)	201(2)	-54(12)	-389(13)	-1(4)
O	-150(39)	35233(12)	41480(18)		2120(61)	159(6)	368(11)	255(29)	-48(45)	-78(12)
C1	15682(48)	18867(14)	30983(20)		1514(63)	112(6)	215(11)	-38(33)	-87(44)	-14(13)
C2	8730(42)	19126(14)	39145(21)		979(54)	141(7)	241(12)	-26(31)	-60(41)	2(14)
C3	6934(52)	13775(17)	43285(27)		1290(63)	147(7)	350(15)	-0(37)	91(52)	53(17)
C4	1149(53)	13795(20)	50858(31)		1359(64)	207(9)	377(17)	-61(38)	163(55)	169(22)
C5	-3322(55)	19241(22)	54354(28)		1676(88)	281(12)	284(15)	-100(47)	334(57)	66(21)
C6	-1791(64)	24584(20)	50327(31)		1456(72)	200(8)	292(12)	-2(36)	244(46)	-37(21)
C7	4036(43)	24620(15)	42688(22)		992(57)	144(7)	256(11)	2(30)	12(38)	-14(15)
C8	5518(44)	30622(16)	38625(22)		1175(56)	141(7)	257(12)	15(33)	-282(45)	-38(14)
C9	13923(48)	30867(15)	30654(20)		1575(67)	117(6)	211(11)	29(33)	-184(45)	39(14)
H1	1288(47)	1525(16)	2866(22)	2,5(,8)						
H3	962(52)	1019(18)	4095(23)	3,0(,8)						
H4	28(50)	1032(18)	5368(24)	2,8(,8)						
H5	-653(64)	1972(22)	5972(31)	4,5(1,1)						
H6	-483(58)	2826(24)	5236(30)	4,8(1,2)						
H9	996(56)	3422(18)	2718(26)	3,9(,9)						

(weighted valve $R_w = 4.7\ \%$) for 1003 observed reflections.

Final fractional coordinates and thermal parameters with estimated standard deviations are given in Table 1. The expression for anisotropic vibration is

$$\exp[-(B11h^2 + B22k^2 + B33l^2 + B12hk + B13hl + B23kl)]$$

The principal axes of the thermal vibration ellipsoids for sulfur, oxygen, and carbon atoms were calculated from the temperature parameters of Table 1. Maximum root mean squares amplitudes range from 0.19 to 0.27 Å. Rigid-body analysis of translational, librational, and screw motion[5] gave relatively large r.m.s. discrepancy between atomic vibration tensor components calculated from the thermal parameters of Table 1 and those calculated from the rigid-body parameters. By including the 22 non-hydrogen atoms the value obtained was 0.0039 Å², not strongly supporting the assumption of

Table 2. Bond distances and angles with estimated standard deviations.

DISTANCE	(Å)	DISTANCE	(Å)	DISTANCE	(Å)
S - C1	1,811(3)	S - C9	1,815(3)	C1 - C2	1,509(5)
C8 - C9	1,523(5)	C1 - C9′	1,577(5)	C2 - C7	1,402(5)
C7 - C8	1,499(5)	O - C8	1,209(4)	C2 - C3	1,384(5)
C3 - C4	1,382(7)	C4 - C5	1,385(7)	C5 - C6	1,370(6)
C6 - C7	1,394(6)				

ANGLE	(°)	ANGLE	(°)
C1 - S - C9	93,6(2)	S - C1 - C2	110,8(2)
S - C9 - C8	108,0(2)	S - C1 - C9′	112,8(2)
S - C9 - C1′	114,0(2)	C2 - C1 - C9′	112,8(3)
C8 - C9 - C1′	113,2(3)	C1 - C2 - C7	122,1(3)
C9 - C8 - C7	119,1(3)	C2 - C7 - C8	122,3(3)
C1 - C2 - C3	119,1(3)	C8 - C7 - C6	118,2(3)
O - C8 - C7	121,3(3)	O - C8 - C9	119,5(3)
C2 - C3 - C4	121,2(4)	C3 - C4 - C5	119,7(4)
C4 - C5 - C6	119,9(4)	C5 - C6 - C7	120,9(4)
C6 - C7 - C2	119,4(3)	C7 - C2 - C3	118,8(3)

DISTANCE	(Å)	DISTANCE	(Å)	DISTANCE	(Å)
C1 - H1	,92(4)	C9 - H9	1,00(4)	C3 - H3	,91(4)
C4 - H4	,91(4)	C5 - H5	,96(5)	C6 - H6	,91(5)

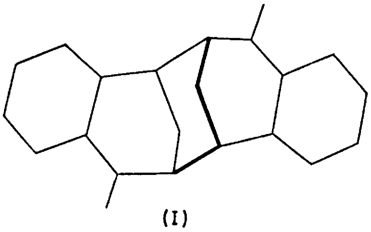
ANGLE	(°)	ANGLE	(°)
H1 - C1 - S	134,(2)	H1 - C1 - C2	111,(2)
H1 - C1 - C9′	105,(2)	H9 - C9 - S	97,(2)
H9 - C9 - C8	116,(3)	H9 - C9 - C1′	107,(3)
H3 - C3 - C2	119,(2)	H3 - C3 - C4	120,(2)
H4 - C4 - C3	122,(3)	H4 - C4 - C5	118,(3)
H5 - C5 - C4	125,(3)	H5 - C5 - C6	115,(3)
H6 - C6 - C5	123,(3)	H6 - C6 - C7	116,(3)

regarding the molecule as an oscillating rigid body. Further, since the maximum libration amplitude was only 3.1°, librational corrections were smaller than one e.s.d., and the coordinates are therefore given with their uncorrected values.

Bond distances and angles are given in Table 2, and Fig. 1 shows the molecule.

The C – S bond lengths of 1.811 and 1.815 Å correspond closely to the single bond (1.816 Å).[6]

The part of the molecule consisting of O,C1, . . . ,C9 is planar to within 0.1 Å with S 1.0 Å out of the plane. The angle between this plane and the one defined by C1,C9,C1′ is 67°. In spite of this tilt of the planar groups, the distance C8 – C2′ of 2.763 Å, and even those of C8 – C3′ (3.251 Å) and C7 – C7′ (3.242 Å), are short and imply repulsions; a fact which is reflected in the bond length C9 – C1′ (1.577 Å) which is significantly longer than the normal C – C single bond. Similar effects have been observed in cage molecules where C – C bonds are lengthened to 1.574(8), 1.572(7),[7] and 1.574(3) Å[8] by cage formation. However, in contradiction to such cases, where the internal strain is forced on the molecules by synthesis, one would, in view of the reaction scheme shown above, expect the *anti* form (I) to be the more stable structure.



(I)

Other bond distances and angles are normal. No short *inter*-molecular contacts are observed. A list of observed and calculated structure factors is available by request to the author.

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