Crystal Structures of two Dimerisation Products of 5-Methylthiopyrylium-3-oxide

P. GROTH

Department of Chemistry, University of Oslo, Oslo 3, Norway

Both isomers of the dimerisation product $(C_6H_6OS)_2$ belong to the monoclinic system with space group $P2_1/c$ and four molecules in the unit cell. The cell dimensions for the *anti* and *syn* isomer, respectively, are
$a = 6.692(1)$ Å, $b = 14.113(3)$ Å, $c = 13.087(3)$ Å, $\beta = 112.15(1)°$
$a = 7.715(3)$ Å, $b = 7.582(2)$ Å, $c = 20.496(4)$ Å, $\beta = 108.25(2)°$
Intensities were recorded on an automatic four circle diffractometer. The structures were solved by direct methods and refined by full-matrix least squares technique:
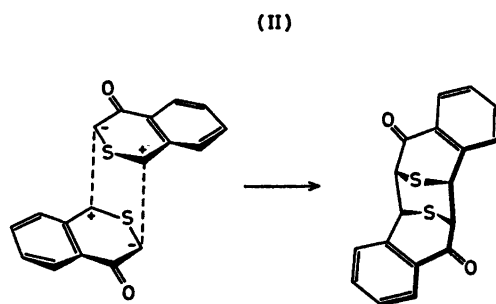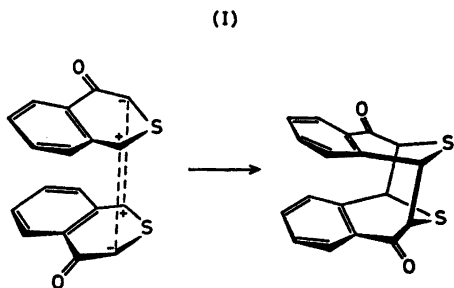*anti*: $R = 4.8$ % ($R_w = 4.2$ %) for 1442 observed reflections;
syn: $R = 4.4$ % ($R_w = 5.7$ %) for 1848 observed reflections.

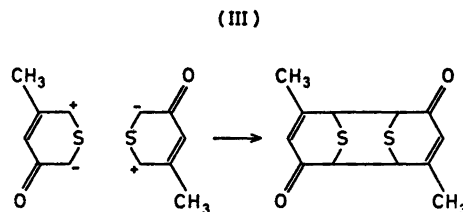The results are compared with those of the major dimerisation product of benzo[c]thiopyrylium-4-oxide.

Dimerisation of thiopyrylium-4-oxide derivates are studied by Undheim *et al.*[1] In the case of benzo[c]thiopyrylium-4-oxide a recent crystal structure investigation[2] revealed that the major product has the *syn* structure. The reaction scheme may be written as in I.

To the minor product (for which no good single crystals yet have been obtained) it seems

(II)

reasonable to assign the *anti* structure with the dimerisation II.

Also in the case of 5-methylthiopyrylium-3-oxide two products are obtained, and it was expected that the dimerisation followed the analogous scheme (III).

(III)

However, the crystal structure determinations presented in this paper show that the scheme for dimerisation of 5-methylthiopyry-
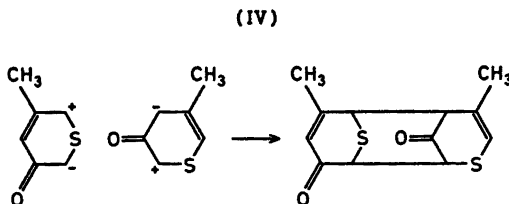
(I)

(IV)

Table 1. Final fractional coordinates and thermal parameters with estimated standard deviations (multiplied by 10^5 for non-hydrogens and 10^4 for hydrogens) for the *anti* isomer. For numbering of atoms, see Fig. 1. Hn is bonded to Cn and Hm,n is bonded to CMm.

ATOM	X	Y	Z	B11	B22	B33	B12	B13	B23
S1	30218(19)	43244(8)	7334(11)	2513(37)	369(7)	699(18)	510(27)	83(32)	-101(15)
S2	75281(17)	32455(8)	6834(9)	2112(31)	381(7)	467(8)	-98(25)	850(25)	115(13)
O1	33600(44)	22112(23)	23170(23)	2569(94)	609(22)	691(25)	-674(75)	1137(83)	-64(37)
O2	36575(50)	12281(23)	-6661(27)	3379(107)	533(21)	695(28)	-415(81)	175(92)	-371(41)
C1	51697(71)	46701(34)	19423(39)	2439(138)	313(27)	793(43)	-184(104)	780(129)	-270(67)
C2	66127(63)	41422(31)	26836(34)	1874(122)	422(29)	543(36)	-238(94)	701(113)	-260(58)
C3	66010(59)	30752(30)	25041(32)	1743(111)	404(28)	348(30)	30(87)	486(97)	87(45)
C4	43409(60)	27115(29)	19452(32)	1766(116)	323(24)	434(32)	-48(85)	789(101)	-156(45)
C5	34134(64)	30464(30)	7516(33)	1657(117)	420(27)	431(31)	-176(92)	344(105)	-19(46)
C6	81323(63)	26906(29)	20191(33)	1833(117)	387(26)	424(32)	-220(89)	308(104)	50(47)
C7	79833(59)	16263(29)	19345(33)	1664(118)	387(26)	585(33)	288(91)	816(103)	97(49)
C8	65384(68)	11779(33)	18592(35)	2554(134)	382(28)	545(35)	42(106)	910(115)	-74(51)
C9	49366(64)	16598(31)	1030(34)	2178(128)	397(26)	473(32)	-84(99)	797(107)	-121(51)
C10	48548(64)	27427(31)	1178(33)	2142(126)	420(27)	300(31)	176(93)	320(103)	103(47)
CM1	83437(90)	45588(43)	36708(46)	2832(174)	685(41)	679(47)	-943(129)	788(147)	-368(66)
CM2	94103(83)	10918(41)	29285(42)	2307(152)	500(35)	653(42)	247(111)	544(134)	308(61)

ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
H1	5211(61)	5336(30)	1999(33)	4.2(1.0)	H11	8252(62)	5263(33)	3659(34)	5.1(1.1)
H3	6958(62)	2761(28)	3272(33)	3.0(1.0)	H12	9940(70)	4415(28)	3742(33)	6.0(1.0)
H5	1998(64)	2788(28)	414(34)	2.1(1.0)	H13	8189(64)	4361(30)	4294(37)	6.6(1.1)
H6	9561(59)	2891(28)	2462(33)	1.3(1.0)	H21	9186(63)	438(31)	2904(34)	6.4(1.1)
H8	6391(61)	519(30)	1047(33)	2.7(1.1)	H22	9081(65)	1267(38)	3563(36)	5.4(1.1)
H10	4267(60)	3013(27)	-581(34)	2.9(1.0)	H23	10922(69)	1244(29)	3059(32)	5.0(1.0)

Table 2. Final fractional coordinates and thermal parameters with estimated standard deviations (multiplied by 10^5 for nonhydrogens and 10^4 for hydrogens) for the *syn* isomer. For numbering of atoms, see Fig. 2. Hn is bonded to Cn and Hm,n is bonded to CMm.

ATOM	X	Y	Z	B11	B22	B33	B12	B13	B23
S1	15575(11)	41865(9)	38909(4)	2524(19)	1193(13)	288(2)	257(23)	165(10)	145(8)
S2	3940(9)	95285(9)	41730(3)	1757(15)	1480(13)	263(2)	378(20)	710(8)	-0(7)
O1	-19404(25)	66100(27)	27508(10)	1582(38)	2289(44)	293(6)	-103(64)	116(25)	145(26)
O2	28073(33)	63008(33)	55162(11)	2816(55)	3441(58)	264(6)	-870(92)	349(29)	657(33)
C1	26393(38)	49710(38)	33159(15)	1670(55)	1646(53)	294(8)	612(90)	163(34)	-376(36)
C2	23575(32)	64696(33)	29662(12)	1224(44)	1663(49)	215(7)	-36(75)	243(28)	-570(33)
C3	10576(30)	78326(31)	30816(12)	1271(42)	1364(42)	187(6)	143(69)	227(25)	100(26)
C4	-5365(33)	68396(31)	31915(12)	1423(48)	1238(43)	213(7)	-200(72)	392(31)	-62(27)
C5	-649(35)	59497(33)	38898(13)	1406(48)	1470(47)	253(7)	-664(78)	340(30)	235(30)
C6	19736(33)	91387(31)	36985(12)	1601(49)	1117(41)	203(6)	-104(72)	567(29)	12(27)
C7	38116(32)	85465(32)	41571(12)	1341(46)	1606(47)	191(6)	-714(75)	386(27)	-292(28)
C8	40205(35)	76107(38)	47247(13)	1416(51)	2069(57)	205(7)	-244(86)	193(30)	-102(32)
C9	28349(36)	69749(35)	49713(12)	1888(54)	1679(48)	181(7)	-597(84)	354(31)	18(29)
C10	9867(34)	72794(34)	44942(13)	1593(46)	1700(49)	214(7)	-542(80)	665(31)	190(30)
CM1	32725(50)	68855(64)	24312(19)	1993(78)	3259(91)	310(10)	-377(129)	847(43)	-631(52)
CM2	54454(44)	91136(61)	39604(17)	1620(59)	3438(98)	269(9)	-1756(123)	621(38)	-435(49)

ATOM	X	Y	Z	B	ATOM	X	Y	Z	B
H1	3401(40)	4141(37)	3256(15)	6.1(.6)	H11	3251(84)	7961(82)	2229(34)	19.3(1.8)
H3	609(38)	8480(35)	2677(15)	3.6(.6)	H12	2901(83)	6394(73)	2152(32)	16.1(1.7)
H5	-990(45)	5370(50)	3954(18)	3.5(.8)	H13	4465(91)	6438(73)	2513(32)	16.7(1.8)
H6	2196(52)	10351(55)	3513(20)	1.2(1.0)	H21	6574(63)	8667(50)	4354(22)	8.5(1.0)
H8	5249(42)	7228(36)	5052(15)	3.7(.6)	H22	5426(60)	10418(67)	3846(24)	9.5(1.2)
H10	-190(66)	7255(52)	4749(23)	4.0(1.0)	H23	5433(58)	8683(53)	3555(24)	8.7(1.0)

Table 3. Bond distances and angles for the *anti* isomer.

DISTANCE	(Å)	DISTANCE	(Å)	DISTANCE	(Å)
S1 - C1	1.759(5)	S1 - C5	1.821(4)	S2 - C10	1.804(4)
S2 - C6	1.816(4)	O1 - C4	1.186(4)	O2 - C9	1.211(4)
C1 - C2	1.312(6)	C2 - C3	1.511(6)	C3 - C4	1.515(5)
C4 - C5	1.522(5)	C2 - CM1	1.499(6)	C7 - CM2	1.496(6)
C3 - C6	1.569(5)	C5 - C10	1.551(6)	C6 - C7	1.507(5)
C7 - C8	1.346(5)	C8 - C9	1.472(6)	C9 - C10	1.530(6)

ANGLE	(°)	ANGLE	(°)
C1 - S1 - C5	101.4(2)	C6 - S2 - C10	93.0(2)
O1 - C4 - C5	122.1(3)	O1 - C4 - C3	124.5(4)
O2 - C9 - C10	119.7(4)	O2 - C9 - C8	122.3(4)
C1 - C2 - CM1	122.1(4)	C3 - C2 - CM1	116.3(4)
C6 - C7 - CM2	115.9(4)	C8 - C7 - CM2	121.4(4)
S1 - C1 - C2	129.2(4)	C1 - C2 - C3	121.6(4)
C2 - C3 - C4	110.9(3)	C3 - C4 - C5	113.4(3)
C4 - C5 - S1	108.8(3)	S2 - C6 - C7	112.0(3)
C6 - C7 - C8	122.5(4)	C7 - C8 - C9	124.4(4)
C8 - C9 - C10	116.0(4)	C9 - C10 - S2	111.3(3)
S1 - C5 - C10	112.5(3)	C4 - C5 - C10	111.6(3)
C2 - C3 - C6	113.7(3)	C4 - C3 - C6	108.4(3)
S2 - C10 - C5	113.1(3)	C9 - C10 - C5	108.4(3)
S2 - C6 - C3	110.9(3)	C7 - C6 - C3	110.0(3)

Table 4. Bond distances and angles for the *syn* isomer.

DISTANCE	(Å)	DISTANCE	(Å)	DISTANCE	(Å)
S1 - C1	1.748(3)	S1 - C5	1.831(3)	S2 - C10	1.817(3)
S2 - C6	1.818(2)	O1 - C4	1.178(3)	O2 - C9	1.186(3)
C1 - C2	1.325(4)	C2 - C3	1.509(3)	C3 - C6	1.518(3)
C4 - C5	1.520(3)	C2 - CM1	1.511(4)	C7 - CM2	1.502(4)
C3 - C6	1.576(3)	C5 - C10	1.554(4)	C6 - C7	1.509(3)
C7 - C8	1.329(4)	C8 - C9	1.471(4)	C9 - C10	1.532(4)

ANGLE	(°)	ANGLE	(°)
C1 - S1 - C5	102.8(1)	C6 - S2 - C10	93.0(1)
O1 - C4 - C5	122.4(2)	O1 - C4 - C3	123.9(2)
O2 - C9 - C10	121.0(2)	O2 - C9 - C8	122.5(2)
C1 - C2 - CM1	122.5(3)	C3 - C2 - CM1	117.1(3)
C6 - C7 - CM2	116.5(2)	C8 - C7 - CM2	120.4(3)
S1 - C1 - C2	128.7(2)	C1 - C2 - C3	120.5(2)
C2 - C3 - C4	107.0(2)	C3 - C4 - C5	113.2(2)
C4 - C5 - S1	106.7(2)	S2 - C6 - C7	111.1(2)
C6 - C7 - C8	123.1(2)	C7 - C8 - C9	125.6(2)
C8 - C9 - C10	116.5(2)	C9 - C10 - S2	109.0(2)
S1 - C5 - C10	115.0(2)	C4 - C5 - C10	112.6(2)
C2 - C3 - C6	113.5(2)	C4 - C3 - C6	112.2(2)
S2 - C10 - C5	110.5(2)	C9 - C10 - C5	114.6(2)
S2 - C6 - C3	108.8(2)	C7 - C6 - C3	114.5(2)

lium-3-oxide is as in IV, and that the major product (as in the case of benzo[c]thiopyrylium-4-oxide) has the *syn* structure.

Both isomers belong to the monoclinic system with space group $P2_1/c$ and four molecules in the unit cell. The cell dimensions for the *anti* and *syn* isomer, respectively, are: $a = 6.692(1)$ Å, $b = 14.113(3)$ Å, $c = 13.087(3)$ Å, $\beta = 112.15(1)°$, $a = 7.715(3)$ Å, $b = 7.582(2)$ Å, $c = 20.496(4)$ Å, $\beta = 108.25(2)°$. With $2\theta(\text{max}) = 50°$ and MoKα radiation, about 2000 independent reflections were measured on an automatic four circle diffractometer for each crystal. Using an observed unobserved cutoff at $2.0\sigma(I)$, 1442 were recorded as observed for the *anti* isomer and 1848 for the *syn* isomer. No corrections have

been made for absorption or secondary extinction effects.

The structures were solved by direct methods [3] and refined by full-matrix least squares technique.[4],* Hydrogen atom positions were calculated. Anisotropic temperature factors were introduced for S, O, and C atoms, and weights in least squares were calculated from the standard deviations in intensities, $\sigma(I)$, taken as

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

where C_T is the total number of counts and C_N the net count (peak minus background). The form factors were those of Hanson *et al.*[5] except for hydrogen.[6] The final R-values arrived at were:

anti: $R = 4.8$ % ($R_w = 4.2$ %) for 1442 observed reflections;

syn: $R = 4.4$ % ($R_w = 5.7$) % for 1848 observed reflections.

Final fractional coordinates and thermal vibration parameters are given in Tables 1 and 2. The expression for anisotropic vibration is:

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

Principal axes of the thermal vibration ellipsoids for sulfur, oxygen, and carbon atoms were calculated from the temperature parameters of Tables 1 and 2. Maximum root mean square

Fig. 1. Schematical drawing of the *anti* isomer.

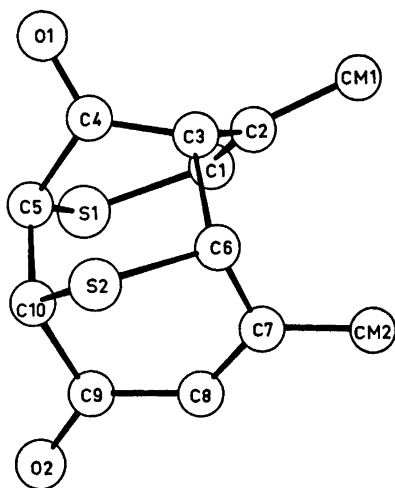* All programs used (except those for phase determination) are included in this reference.

Fig. 2. Schematical drawing of the *syn* isomer.

amplitudes range from 0.20 to 0.35 Å. Rigid-body analyses of translational, librational, and screw motion [7] gave relatively large r.m.s. discrepancies between atomic vibration tensor components calculated from the thermal parameters of Tables 1 and 2, and those calculated from the rigid-body parameters. By including all 16 non-hydrogen atoms, the values obtained for the *anti*- and *syn* isomer, respectively, were 0.0040 and 0.0036 Å². These numbers do not strongly support the assumption of regarding the molecules as oscillating rigid-bodies, and the coordinates were therefore not corrected for librational motion.

Interatomic distances and bond angles are given in Tables 3 and 4. The standard deviations (in parentheses) are estimated from the correlation matrix of the last least squares refinement cycle. Figs. 1 and 2 are schematical drawings of the molecules.

From Tables 1 and 2 it may be seen that the only possibly significant difference in bond length is that of O2 – C9 which is 0.025 Å longer for the *anti* isomer. The S1 – C1 bonds as well as the other sulfur carbon bond distances correspond closely to normal values for S – C(sp^2) and S – C(sp^3), respectively.[8,9] The C3 – C6 bonds seem to be somewhat longer than C5 – C6 (and significantly longer than a normal C – C single bond). This effect has also been observed in the case of the major dimerisa-

tion product of benzo[c]thiopyrylium-4-oxide [2] (C – C = 1.577 Å).

When comparing the angles of Table 3 with those of Table 4 some differences may be observed. C2 – C3 – C6, C3 – C6 – C7, S1 – CS – C10, and C5 – C10 – C9 are somewhat larger for the *syn* isomer, possibly due to repulsions between the methyl groups which are separated by a distance of only 3.49 Å. The angles C6 – S2 – C10 have approximately the same value as that of the major dimerisation product of benzo[c]thiopyrylium-4-oxide [2] (93.6°), while the C1 – S1 – C5 angles correspond to the three C – S – C angles in a cyclisation product of 6-chloropyrid-2-thione [9] (102.4, 101.0, 101.8°). The ring angles at the carbonyl group C4 = O1 may be compared with values found in the crystals of cyclohexane-1,4-dione,[10] and the latter are seen to be about four degrees larger (117.5, 117.3°).

C – H distances range from 0.90 to 1.05 Å. Except for a close contact (3.55 Å) between centrosymmetrically related CM1-atoms of the *anti* isomer no short *inter*-molecular distances are observed.

Lists of observed and calculated structure factors are available by request to the author.

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