

PREPARATION AND ASSIGNMENT OF SELENIUM ANALOGES OF BENZO-1,2-DITHIOLE-3-THIONE

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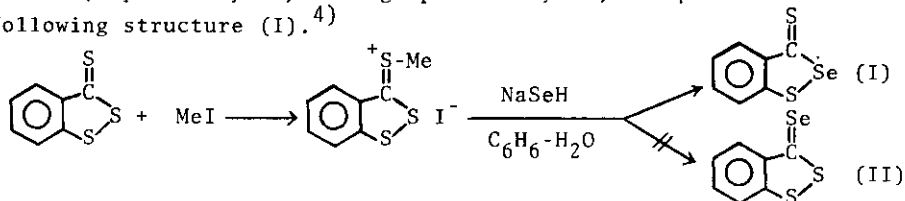
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The product formed in the reaction of benzo-3-methylthio-1,2-dithiolium iodide with sodium hydrogen selenide was assigned as benzo-1,2-thiaselenole-3-thione(I) by X-ray crystallographic techniques. (I) crystallizes in a monoclinic space group $P2_1/c$ with $a=13.01$, $b=4.10$, $c=28.51$ Å, $\beta=90.50^\circ$ and $Z=8$. While, treatment of benzo-3-chloro-1,2-dithiolium perchlorate with sodium O,O-diethyl phosphoro-selenate gave benzo-1,2-dithiole-3-selone(II) in a moderate yield. The structure of the compound(II) has also been confirmed by X-ray crystallographic techniques. (II) crystallizes in a monoclinic space group $P2_1/c$ with $a=4.06$, $b=10.83$, $c=17.75$ Å, $\beta=98.81^\circ$ and $Z=4$. Selone(II) was isomerized to the thione(I) thermally, whereas the latter (I) was not converted to any other product.

Derivatives of benzotrithiones prepared by the reaction of appropriate olefins with elemental sulfur at high temperatures have been known to be quite stable.¹⁾ Syntheses of similar selenium analoges have also been attempted.²⁾ However, introduction of selenium into three possible positions of trithione appears to be limited only to the following three cases (1-, 1,2- or 1,2,3- positions), while no well-characterized synthetic route for 1-, 2- or 3-selene derivatives of the trithione have been elucidated.

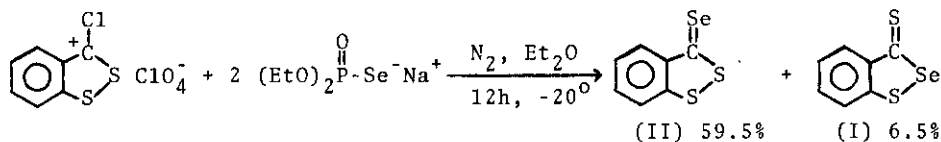
In this paper, we wish to report the synthesis and characterization of 2- and 3-selene derivatives of benzotrithione.

In our early study, we found the reaction of benzo-3-methylthio-1,2-dithiolium iodide with sodium hydrogen selenide afforded a certain selene derivative. On the basis of the elemental analysis, UV and IR alone, the structure of this material was assigned erroneously to the following structure(II).³⁾ However, upon X-ray crystallographic analysis, the product was shown to have following structure (I).⁴⁾



This compound (I) crystallizes in a monoclinic space group $P2_1/c$ with $a=13.01$, $b=4.1$, $c=28.51 \text{ \AA}$, $\beta=90.50^\circ$ and $Z=8$ ($R=0.11$). Intensity data were collected on a Rigaku automatic fourcircle diffractometer using Zr-filtered Mo-K α radiation in the ω - 2θ scanning mode at a speed of 4° min^{-1} in $\theta(2\theta < 46^\circ)$. Positional and thermal parameters for the non-hydrogen atoms, and principal bond lengths and bond angles are listed in Tables I and II, respectively.

Therefore, we have carried out several experiments and finally succeeded in the synthesis of (II) by treatment of benzo-3-chloro-1,2-dithiolium perchlorate with sodium O,O-diethyl phosphoroselenate.



A heterogeneous mixture of benzo-3-chloro-1,2-dithiolium perchlorate⁵⁾ and sodium O,O-diethyl phosphoroselenate⁶⁾ in dry ether was stirred vigorously under nitrogen atmosphere at $-20 \sim -30^\circ$. After 12 h, the reaction mixture was filtered and the solvent was removed under reduced pressure at 0° . The residual material was chromatographed through silica-gel column at 0° using benzene-hexane(1:3) as eluent. A dark greenish brown solution was obtained and the solvent was evaporated. The product thus formed was purified by column chromatography under the same condition as described above (yield:59.5%). The structure of the compound(II) has been determined by X-ray crystallographic techniques.⁸⁾ The new seleno compound (II) crystallizes in a monoclinic space group $P2_1/c$ with $a=4.06$, $b=10.83$, $c=17.75 \text{ \AA}$, $\beta=98.81^\circ$ and $Z=4$ and an observed density of (II) was 1.99 g cm^{-3} . Positional and thermal parameters for the atom, and principal bond lengths and bond angles are presented in Tables III and IV, respectively. Moreover, the structure of the materials was assigned to have the formulas(I) and (II) on the basis of elemental analysis, Mass, UV and IR (See Table V).

Table V. Physical Data of Benzo-1,2-thiaselenole-3-thione(I) and Benzo-1,2-dithiole-3-selone(II).

mp ($^\circ\text{C}$)	83-84	112-113
IR (KBr, cm^{-1})	1575, 1440, 1422, 1265, 1235 1125, 1010(C=S), 850, 750	1575, 1430, 1275, 1234, 940(C=Se) ⁷⁾ 905, 750, 710
UV (nm, CH_3CN)	445(shoulder), 462($\epsilon=1320$)	465($\epsilon=3400$), 490($\epsilon=2670$)
Mass (m/e, ^{80}Se)	232(M^+ , 96.9%), 230(46.5%) 188(M^+CS , 17.0%), 184(5.7%) 152(M^+Se , 19.2%), 120(M^+SeS , 100%), 108(M^+CSeS , 24.5%) 76(M^+CS_3 , 5.0%)	232(M^+ , 100%), 230(46.5%) 188(M^+CS , 22.6%), 184(10.7%) 152(M^+Se , 22.0%), 120(M^+SeS , 91.2%) 108(M^+CSeS , 27.7%), 76(M^+CS_3 , 3.1%)
elemental analysis	C: 36.59 H: 1.70 Calcd. for $\text{C}_7\text{H}_4\text{S}_2\text{Se}$; C: 36.37 H: 1.74	C: 36.38 H: 1.75

Table I Positional and Thermal Parameters for the Non-hydrogen atoms of (I).

The Thermal Parameters ($\times 10^4$) are defined by $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.
 Estimated Standard Deviations are given in Parenthesis.

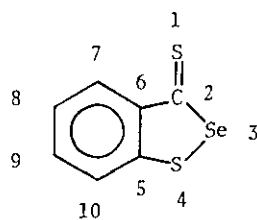
Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	0.3962 (4)	0.1958 (16)	0.1151 (2)	45 (3)	809 (45)	13 (1)	-22 (21)	-5 (2)	-6 (10)
C(2)	0.2913 (13)	0.0752 (51)	0.0880 (6)	43 (11)	589 (142)	8 (2)	27 (71)	18 (8)	-7 (32)
Se(3)	0.1637 (1)	0.1695 (6)	0.1165 (1)	49 (1)	653 (15)	11 (0)	43 (8)	4 (1)	5 (4)
S(4)	0.0735 (5)	-0.0605 (13)	0.0598 (2)	33 (3)	548 (35)	12 (1)	14 (17)	3 (2)	4 (8)
C(5)	0.1824 (14)	-0.1716 (54)	0.0274 (6)	58 (13)	693 (157)	5 (2)	-109 (79)	3 (8)	48 (32)
C(6)	0.2812 (12)	-0.0860 (42)	0.0452 (6)	38 (11)	324 (109)	8 (2)	30 (59)	10 (8)	60 (27)
C(7)	0.3658 (13)	-0.1871 (47)	0.0178 (6)	50 (12)	443 (127)	9 (2)	124 (68)	-11 (9)	36 (30)
C(8)	0.3502 (16)	-0.3667 (60)	-0.0230 (7)	69 (15)	765 (179)	11 (3)	63 (90)	8 (10)	15 (39)
C(9)	0.2547 (16)	-0.4336 (55)	-0.0397 (6)	79 (16)	611 (157)	8 (2)	-12 (87)	-4 (10)	-11 (34)
C(10)	0.1661 (14)	-0.3472 (54)	-0.0145 (7)	48 (13)	570 (150)	14 (3)	115 (76)	7 (10)	32 (37)
S(1')	0.9338 (4)	0.4144 (15)	0.1547 (2)	42 (3)	719 (41)	11 (1)	-2 (19)	12 (2)	-10 (9)
C(2')	0.8586 (14)	0.2993 (46)	0.1982 (7)	48 (12)	386 (121)	12 (3)	111 (67)	-5 (9)	24 (31)
Se(3')	0.8925 (2)	0.4038 (5)	0.2600 (1)	54 (1)	551 (14)	12 (0)	6 (7)	0 (1)	-12 (3)
S(4')	0.7535 (4)	0.1802 (13)	0.2888 (2)	53 (3)	552 (35)	7 (1)	-10 (18)	7 (2)	-3 (8)
C(5')	0.7064 (13)	0.0385 (42)	0.2352 (5)	52 (12)	323 (110)	5 (2)	78 (62)	6 (8)	29 (25)
C(6')	0.7623 (12)	0.1143 (41)	0.1934 (6)	37 (10)	282 (106)	9 (2)	-92 (58)	6 (8)	10 (27)
C(7')	0.7249 (16)	0.0135 (50)	0.1495 (6)	82 (16)	471 (138)	8 (2)	-27 (79)	-16 (10)	18 (31)
C(8')	0.6300 (14)	-0.1523 (51)	0.1465 (7)	51 (13)	487 (138)	14 (3)	48 (73)	-15 (10)	0 (36)
C(9')	0.5784 (14)	-0.2201 (45)	0.1884 (7)	47 (12)	272 (114)	17 (3)	-101 (64)	0 (10)	-34 (33)
C(10')	0.6117 (13)	-0.1382 (51)	0.2315 (7)	33 (11)	527 (140)	14 (3)	-26 (67)	0 (9)	12 (35)

Table II. Bond Lengths and Bond Angles of Molecule (I).

Estimated Standard Deviations are given in Parenthesis.

S(1) - C(2)	1.646 (15)	S(1) - C(2) - Se(3)	119.0 (6)
C(2) - Se(3)	1.878 (15)	S(1) - C(2) - C(6)	127.5 (9)
C(2) - C(6)	1.432 (20)	Se(3) - C(2) - C(6)	113.4 (8)
Se(3) - S(4)	2.198 (4)	C(2) - Se(3) - S(4)	93.7 (4)
S(4) - C(5)	1.749 (15)	Se(3) - S(4) - C(5)	94.7 (4)
C(5) - C(6)	1.428 (20)	S(4) - C(5) - C(6)	118.6 (10)
C(5) - C(10)	1.420 (20)	S(4) - C(5) - C(10)	119.7 (10)
C(6) - C(7)	1.409 (20)	C(6) - C(5) - C(10)	121.5 (10)
C(7) - C(8)	1.396 (20)	C(2) - C(6) - C(5)	119.4 (10)
C(8) - C(9)	1.379 (20)	C(2) - C(6) - C(7)	122.6 (10)
C(9) - C(10)	1.375 (20)	C(5) - C(6) - C(7)	118.0 (10)
	(A)	C(6) - C(7) - C(8)	120.0 (10)
		C(7) - C(8) - C(9)	119.8 (10)
		C(8) - C(9) - C(10)	123.3 (10)
		C(5) - C(10) - C(9)	116.9 (10)

(degree)



(I)

Table III. Positional and Thermal Parameters for the Atoms of (II).

Anisotropic Temperature Factors ($\times 10^4/\text{\AA}^2$) expressed in the Form

$$\exp[-2\pi^2(U_{11}a^{*2}h^2+U_{22}b^{*2}k^2+U_{33}c^{*2}l^2+2U_{12}a^*b^*hk+2U_{13}a^*c^*hl+2U_{23}b^*c^*kl)].$$

Estimated Standard Deviations are given in Parenthesis.

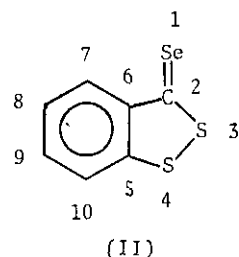
Atom	x	y	z	σ	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Se(1)	0.1871	2.5537	5.6539	(0.0004)	0.0832(3)	0.0618(2)	0.0285(2)	-0.0083(2)	0.0099(2)	-0.0064(1)
C(2)	0.5097	1.9473	3.9969	(0.0030)	0.0388(13)	0.0367(13)	0.0294(12)	-0.0074(11)	0.0017(10)	0.0016(10)
S(3)	1.3313	0.4459	3.8621	(0.0008)	0.0455(4)	0.0345(3)	0.0358(3)	0.0008(3)	0.0067(3)	0.0059(3)
S(4)	1.3252	0.3061	1.7950	(0.0009)	0.0576(5)	0.0372(4)	0.0424(4)	-0.0018(3)	0.0169(4)	-0.0109(3)
C(5)	0.5217	1.8271	1.5715	(0.0031)	0.0436(15)	0.0383(13)	0.0308(12)	-0.0111(12)	0.0086(11)	-0.0054(11)
C(6)	0.1664	2.5494	2.7273	(0.0030)	0.0359(14)	0.0333(12)	0.0237(13)	-0.0067(10)	0.0051(11)	-0.0041(9)
C(7)	-0.5159	3.7571	2.5989	(0.0034)	0.0448(15)	0.0409(14)	0.0388(14)	0.0001(13)	0.0021(12)	-0.0021(11)
C(8)	-0.8246	4.2429	1.3348	(0.0041)	0.0526(18)	0.0493(16)	0.0559(18)	-0.0005(16)	-0.0036(15)	0.0117(16)
C(9)	-0.4425	3.5254	0.2124	(0.0041)	0.0572(20)	0.0599(19)	0.0370(15)	-0.0105(17)	-0.0046(14)	0.0095(14)
C(10)	0.2227	2.3291	0.2985	(0.0042)	0.0626(21)	0.0595(18)	0.0248(13)	-0.0197(16)	0.0047(13)	-0.0031(13)
U										
H(7)	0.0567	Isotropic Temperature Factor:								
H(8)	0.0631	$\exp(-8\pi^2U\sin^2\theta/\lambda^2)$								
H(9)	0.0617									
H(10)	0.0564									

Table IV. Bond Lengths and Bond Angles of Molecule (II).

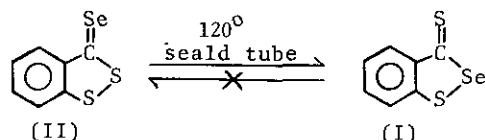
Estimated Standard Deviations are given in Parenthesis.

Se(1) - C(2)	1.794 (3)	Se(1) - C(2) - S(3)	117.0 (0.2)
C(2) - S(3)	1.717 (3)	Se(1) - C(2) - C(6)	128.9 (0.2)
C(2) - C(6)	1.446 (4)	S(3) - C(2) - C(6)	114.1 (0.2)
S(3) - S(4)	2.072 (1)	C(2) - S(3) - S(4)	97.8 (0.1)
S(4) - C(5)	1.735 (3)	S(3) - S(4) - C(5)	94.1 (0.1)
C(5) - C(6)	1.408 (4)	S(4) - C(5) - C(6)	117.4 (0.2)
C(5) - C(10)	1.401 (5)	S(4) - C(5) - C(10)	122.0 (0.3)
C(6) - C(7)	1.393 (5)	C(6) - C(5) - C(10)	120.5 (0.3)
C(7) - C(8)	1.389 (5)	C(2) - C(6) - C(5)	116.5 (0.3)
C(8) - C(9)	1.385 (6)	C(2) - C(6) - C(7)	123.9 (0.3)
C(9) - C(10)	1.371 (6)	C(5) - C(6) - C(7)	119.5 (0.3)
H(7) - C(7)	1.082 (41)	C(6) - C(7) - C(8)	119.7 (0.3)
H(8) - C(8)	1.078 (41)	C(7) - C(8) - C(9)	119.6 (0.4)
H(9) - C(9)	1.083 (41)	C(8) - C(9) - C(10)	122.4 (0.4)
H(10) - C(10)	1.080 (41)	C(5) - C(10) - C(9)	118.2 (0.4)
	(\AA)	C(6) - C(7) - H(7)	120.3 (2.2)
		C(8) - C(7) - H(7)	120.0 (2.2)
		C(7) - C(8) - H(8)	120.4 (2.2)
		C(9) - C(8) - H(8)	120.0 (2.2)
		C(8) - C(9) - H(9)	118.9 (2.2)
		C(10) - C(9) - H(9)	118.7 (2.2)
		C(5) - C(10) - H(10)	120.9 (2.2)
		C(9) - C(10) - H(10)	121.0 (2.2)

(degree)



In order to examine the thermal stability of benzo-1,2-thiaselenole-3-thione (I) and benzo-1,2-dithiole-3-selone(II), these compounds were pyrolyzed at 120° for 30 min. Upon cooling, these samples were subjected to TLC and UV measurements. The latter(II) was found to be isomerized to the former(I) in 68.2%, recovering a trace of the original seleno compound, whereas the former(I) was not converted to any other product. (See Mass data too)



Thus the exo-seleno isomer seems to be markedly less stable than the endo isomer. The difference in thermal stabilities of these compounds is quite remarkable and may be due to the difference of aromaticities of these two heterocyclic 6 π -electron systems.

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- 8) X-ray data of the compound(II) was given by Dr. Motoo Shiro.

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