Structures of Bis(phenylthio/seleno)dibenzothio/selenophenes with Short Intramolecular S···S and Se···Se Contacts

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The crystal structures of 1-phenylsulfinyl-9-phenylthiodibenzothiophene (**1**), 1,9-bis(phenylthio)dibenzothiophene (**2**), 1,9-bis(phenylthio)dibenzoselenophene (**3**), and 1,9-bis(phenylseleno)dibenzoselenophene (**4**) have been determined by an X-ray method in order to investigate the existence of a short intramolecular S···S or Se···Se contact. The crystal data are: **1**, $C_{24}H_{16}OS_3$, M_w=416.59, Monoclinic, $P2_1/n$, a=9.980(4), b=8.843(4), c=21.933(9) Å, β=92.20(4)°, V=1934(1) Å^3, Z=4, R=0.028, wR=0.027 for 2899 observed reflections. **2**, $C_{24}H_{16}S_3$, M_w=400.59, Monoclinic, $P2_1/n$, a=17.862(2), b=8.050(2), c=13.549(2) Å, β=95.74(1)°, V=1938.4(5) Å^3, Z=4, R=0.053, wR=0.075 for 3251 refined reflections (R=0.057 for 3256 observed reflections). **3**, $C_{24}H_{16}S_2Se$, M_w=447.48, Monoclinic, $P2_1/n$, a=17.899(4), b=8.086(2), c=13.631(2) Å, β=96.33(2)°, V=1960.8(7) Å^3, Z=4, R=0.046, wR=0.070 for 2818 refined reflections (R=0.050 for 2822 observed reflections). **4**, $C_{24}H_{16}Se_3$, M_w=541.27, Monoclinic, $P2_1/n$, a=18.094(2), b=8.1571(6), c=13.723(1) Å, β=96.51(1)°, V=2012.4(3) Å^3, Z=4, R=0.066, wR=0.066 for 3095 refined reflections (R=0.067 for 3096 observed reflections). The nonbonding distances between two S atoms of phenylthio groups are 3.016(1), 3.012(1), and 2.973(1) Å for **1**, **2**, and **3**, respectively. The distance of Se···Se of **4** is 3.070(1) Å. These distances correspond to 82.0, 81.8, 80.8, and 76.8% of the sum of the van der Waals radii for **1**, **2**, **3**, and **4**, respectively. Dibenzothiophene frameworks show severe deformation based on the steric effect of the 1,9-disubstituents. The dihedral angles between the benzene rings and the thiophene/selenophene rings are 6.6—8.5°. Two S/Se atoms of the phenylthio/seleno groups deviate from the thiophene/selenophene ring by about 1 Å on the opposite sides from each other.

In addition typical hypervalent compounds[1] such as σ-sulfuranes[2] and thiathiophthenes,[3] S···N, S···O, and S···S intramolecular nonbonding contacts are often observed in organic sulfur compounds. S-substituted dibenzothiazocinium salts and thiazocine S-oxide show transannular S···N bonds (2.09—2.60 Å) of the σ-sulfurane type.[4] Some sulfur-bonded 1-thionia-5-thiacyclooctane salts and 1,5-dithiacyclooctanes have been found to have a relatively short transannular S···S contact in the range of 3.121—3.271 Å because of the hypervalency of the sulfur atom.[5] Even the existence of S^+–S^+ and Se^+–Se^+ bonds has been confirmed in 1,5-dithioniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate) and 1,5-diselenoniabicyclo[3.3.0]octane tetrafluoroborate by X-ray analyses, in which the lengths of the S^+–S^+ and Se^+–Se^+ bonds are only slightly longer than the normal single bond.[6] However, in the case of trithia compounds, such as 2,6-bis(methylthiomethyl)phenyl phenyl sulfoxide and 9,18-epithio-2,11-dithia[3.3]metacyclophane, the S···S contacts are 3.44 and 3.77 Å, respectively; no hypervalent transannular interactions between S atoms have been observed.[7] In the case of 1-phenylsulfinyl-9-phenylthiodibenzothiophene (**1**) and 1,9-bis(phenylthio)dibenzothiophene (**2**)[8] with rigid and flat dibenzothiophene frameworks, very short S···S contacts (about 2.4 Å) would be expected if the dibenzothiophene moieties are completely planar. In order to investigate the possibility of short S···S contacts and the effect of an electronegative O atom of **1**, the structures of **1** and **2** were determined by an X-ray method. 1,9-Bis(phenylthio)dibenzoselenophene (**3**) and 1,9-bis(phenylseleno)dibenzoselenophene (**4**)[9] have also been determined in order to compare the effect of the thiophene and selenophene rings and the S···S and Se···Se contacts.

Experimental

The crystal data, as well as details concerning the data collection and the structure refinement are listed in Table 1. Intensity data were collected using Rigaku AFC-4 and AFC-5R diffractometers with graphite monochromators. Absorption corrections were applied numerically. The

Table 1. Crystal Data, Details of Data Collection and Structure Refinement

	1	2	3	4
	$C_{24}H_{16}OS_3$	$C_{24}H_{16}S_3$	$C_{24}H_{16}S_2Se$	$C_{24}H_{16}Se_3$
Color	Colorless	Colorless	Colorless	Colorless
Crystal shape	Prisms	Prisms	Prisms	Prisms
M_w	416.59	400.59	447.48	541.27
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	9.980(4)	17.862(2)	17.899(4)	18.094(2)
b/Å	8.843(4)	8.050(2)	8.086(2)	8.1571(6)
c/Å	21.933(9)	13.549(2)	13.631(2)	13.723(1)
β/°	92.20(4)	95.74(1)	96.33(2)	96.51(1)
V/Å^3	1934(1)	1938.4(5)	1960.8(7)	2012.4(3)
Z	4	4	4	4
D_x/Mg m^{-3}	1.431	1.373	1.516	1.787
Crystal size/mm	0.25×0.25×0.32	0.37×0.25×0.22	0.48×0.27×0.34	0.20×0.30×0.40
Diffractometer	AFC-5R	AFC-4	AFC-5R	AFC-5R
Radiation	Cu $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
λ/Å	1.54178	0.71069	0.71069	0.71069
μ/mm^{-1}	3.538	0.372	2.104	5.434
Temperature/K	298	298	298	298
For cell parameters				
2θ range/°	50.5—60.0	25.2—34.4	22.6—34.2	25.0—34.0
No. of reflections	25	25	25	25
Scan range 2θ/°	2—130	2—55	2—55	2—55
Scan width $\Delta\omega$/°	1.5+0.25 tan θ	1.3+0.4 tan θ	1.3+0.5 tan θ	1.5+0.5 tanθ
Scan speed 2θ/° min^{-1}	8—4	4	8—4	8
Scan mode	2θ–ω	2θ–ω	2θ–ω	2θ–ω
Monitored reflections	−4 0 0, 0 0 −10,	0 0 4, 6 0 2	5 0 −5, 7 0 3	1 4 0, 6 0 0
(every 50 reflections)	0 4 0 (50)	0 4 0 (50)	0 4 0 (100)	1 0 5 (50)
Variation of intensities	0.970—1.006	0.959—1.000	0.984—1.009	0.997—1.006
Range of h,k,l	−12—0 0—11	0—24 0—11	−23—23 0—11	−24—24 0—11
	−26—26	−18—18	0—18	0—18
Time for back-ground/s	5—10	10	5—10	10
Transmission factor				
A_{min}—A_{max}	0.395—0.522	0.883—0.931	0.375—0.536	0.131—0.391
No. of reflections				
Measured	4086	5296	5027	5114
Unique	3300	4460	4875	4820
Observed ($\|F_o\|>3\sigma(F)$)	2899	3256	2822	3096
Refined[a)]	2899	3251	2818	3095
R_{int}	0.007	0.027	0.032	0.072
R	0.028	0.053	0.046	0.066
wR	0.027	0.075	0.070	0.066
R(all observed)	0.028	0.057	0.050	0.067
$\Delta\rho_{min}$—$\Delta\rho_{max}$/eÅ^{-3}	−0.222—0.241	−0.371—0.341	−0.758—0.399	−1.452—0.747
$(\Delta/\sigma)_{max}$	0.012	0.036	0.056	0.070
S	1.064	1.044	0.800	1.919

a) Five reflections (10−3, 31−2, 020, 004, and 103) for **2**, four reflections (200, 103, 004, and 020) for **3**, and one reflection (020) for **4**, which were considered to be affected by extinction effects, were omitted from the refinements.

structures were solved using the program MULTAN78.[10] For **1** and **2**, H atoms were found from D-maps. For **3**, some H atoms were located from D-maps; positional parameters of the remaining H atoms were assumed based on calculations, which were included in refinements. For **4**, the positional parameters of H atoms were assumed based on calculations and were included in refinements. The structures were refined using a block-diagonal least-squares method with anisotropic temperature factors for non-H atoms and isotropic ones for H. $\Sigma w(|F_c|-k^{-1}|F_o|)^2$ was minimized. $w=1/(1.20669-0.07370|F_o|+0.00130|F_o|^2)$, $1/\{\sigma^2(F)+0.00274|F_o|^2\}$, $1/\{\sigma^2(F)+0.00604|F_o|^2\}$ and $1/\{\sigma^2(F)+0.00040|F_o|^2\}$ for **1**, **2**, **3**, and **4**, respectively. The final R values were 0.028, 0.057, 0.050, and 0.067 for 2899, 3256, 2822, and 3096 observed reflections for **1**, **2**, **3**, and **4**, respectively. The final atomic parameters are given in Table 2.[11] Atomic scattering factors were taken from International Tables for X-Ray Crystallography.[12] All computations were performed on an IBM 180S Computer of the Data Processing Center of the University of Electro-Com-

Table 2. Positional Parameters and Equivalent Isotropic Temperature Factors (B_{eq}) for Non-H Atoms

Atom	x	y	z	B_{eq}[a)]/Å^2	Atom	x	y	z	B_{eq}[a)]/Å^2
(**1**)					(**3**)				
S(1)	0.41402(5)	0.35879(5)	0.07725(2)	3.14(1)	Se(1)	0.20887(3)	0.98693(5)	0.65388(4)	4.21(1)
S(2)	0.48441(5)	0.96040(5)	0.10168(2)	3.08(1)	S(2)	0.27584(6)	0.41846(13)	0.46573(8)	3.76(3)
S(3)	0.74108(4)	0.83998(5)	0.05176(2)	2.73(1)	S(3)	0.41442(6)	0.50113(12)	0.59746(8)	3.56(3)
O(1)	0.84579(12)	0.80697(15)	0.00639(6)	3.67(3)	C(1)	0.3034(2)	0.9352(5)	0.6151(3)	3.30(10)
C(1)	0.57262(17)	0.43517(20)	0.09356(8)	2.91(4)	C(2)	0.3119(2)	0.7675(4)	0.5933(3)	2.74(8)
C(2)	0.57695(16)	0.59411(19)	0.08596(7)	2.53(4)	C(3)	0.2416(2)	0.6729(5)	0.5915(3)	2.93(9)
C(3)	0.44298(16)	0.65500(20)	0.07206(7)	2.58(4)	C(4)	0.1835(2)	0.7618(5)	0.6292(3)	3.31(10)
C(4)	0.34941(17)	0.53856(20)	0.06177(7)	2.75(4)	C(5)	0.1140(3)	0.6945(6)	0.6407(3)	4.33(12)
C(5)	0.21596(17)	0.56474(22)	0.04351(8)	3.26(5)	C(6)	0.1005(3)	0.5334(6)	0.6137(4)	4.57(13)
C(6)	0.17356(17)	0.71159(23)	0.03699(8)	3.53(5)	C(7)	0.1546(3)	0.4451(6)	0.5682(3)	4.09(12)
C(7)	0.26022(18)	0.83010(22)	0.05166(8)	3.39(5)	C(8)	0.2228(2)	0.5166(5)	0.5523(3)	3.26(9)
C(8)	0.39240(16)	0.80434(19)	0.07074(8)	2.70(4)	C(9)	0.3620(3)	1.0507(5)	0.6162(3)	3.92(11)
C(9)	0.68582(19)	0.35024(21)	0.10890(9)	3.49(5)	C(10)	0.4319(3)	0.9950(5)	0.5965(3)	4.04(11)
C(10)	0.80716(19)	0.42156(23)	0.11585(9)	3.83(5)	C(11)	0.4440(3)	0.8276(6)	0.5837(3)	3.83(11)
C(11)	0.81768(17)	0.57469(22)	0.10306(9)	3.43(5)	C(12)	0.3863(2)	0.7117(5)	0.5855(3)	3.01(9)
C(12)	0.70586(16)	0.66010(20)	0.08729(7)	2.76(4)	C(21)	0.2197(2)	0.4609(5)	0.3523(3)	2.92(9)
C(21)	0.42407(17)	0.97443(20)	0.17678(8)	2.93(4)	C(22)	0.1537(2)	0.5489(6)	0.3420(3)	3.63(10)
C(22)	0.33140(19)	0.87958(23)	0.20159(9)	3.82(5)	C(23)	0.1160(3)	0.5708(7)	0.2480(4)	4.71(13)
C(23)	0.29599(21)	0.89999(27)	0.26132(9)	4.61(6)	C(24)	0.1430(3)	0.5053(7)	0.1663(4)	5.27(15)
C(24)	0.35144(22)	1.01236(27)	0.29621(9)	4.62(6)	C(25)	0.2091(3)	0.4195(9)	0.1771(4)	5.57(17)
C(25)	0.44337(23)	1.10849(26)	0.27168(10)	4.76(6)	C(26)	0.2482(3)	0.3949(6)	0.2698(3)	4.37(12)
C(26)	0.48033(20)	1.08940(23)	0.21231(9)	3.94(5)	C(31)	0.4788(2)	0.5141(5)	0.7068(3)	3.11(9)
C(31)	0.83167(17)	0.92743(21)	0.11576(9)	3.20(5)	C(32)	0.4648(2)	0.6091(5)	0.7874(3)	3.45(10)
C(32)	0.94425(19)	1.01044(23)	0.10233(10)	4.13(5)	C(33)	0.5133(3)	0.6029(6)	0.8747(3)	4.62(13)
C(33)	1.01581(21)	1.08263(27)	0.14850(13)	5.50(7)	C(34)	0.5751(3)	0.4977(7)	0.8807(4)	5.82(17)
C(34)	0.97375(25)	1.07532(29)	0.20754(13)	6.07(8)	C(35)	0.5885(3)	0.4024(7)	0.8013(5)	5.76(16)
C(35)	0.86155(25)	0.99499(30)	0.22065(11)	5.46(7)	C(36)	0.5407(3)	0.4108(6)	0.7129(4)	4.32(12)
C(36)	0.78907(20)	0.91860(25)	0.17500(9)	4.09(5)					
(**2**)					(**4**)				
S(1)	0.20663(5)	0.97865(10)	0.65046(7)	4.46(2)	Se(1)	0.20853(5)	0.96483(11)	0.65812(6)	4.46(3)
S(2)	0.27383(4)	0.41656(10)	0.46885(5)	3.76(2)	Se(2)	0.27337(5)	0.39130(11)	0.45869(5)	3.93(2)
S(3)	0.41500(4)	0.51316(10)	0.59627(6)	3.61(2)	Se(3)	0.41461(5)	0.46901(10)	0.59676(6)	3.62(2)
C(1)	0.2971(2)	0.9411(4)	0.6178(2)	3.45(7)	C(1)	0.3017(4)	0.9149(9)	0.6182(5)	3.49(21)
C(2)	0.3090(2)	0.7720(3)	0.5949(2)	2.92(6)	C(2)	0.3089(4)	0.7459(9)	0.5943(4)	2.86(19)
C(3)	0.2394(1)	0.6771(3)	0.5922(2)	2.95(6)	C(3)	0.2394(4)	0.6558(9)	0.5921(4)	2.99(19)
C(4)	0.1812(2)	0.7715(4)	0.6283(2)	3.52(7)	C(4)	0.1820(4)	0.7431(9)	0.6303(5)	3.43(21)
C(5)	0.1102(2)	0.7060(4)	0.6392(2)	4.27(9)	C(5)	0.1127(5)	0.6786(11)	0.6396(6)	4.23(24)
C(6)	0.0962(2)	0.5426(5)	0.6135(3)	4.67(9)	C(6)	0.0973(5)	0.5208(11)	0.6112(6)	4.74(26)
C(7)	0.1503(2)	0.4512(4)	0.5694(2)	4.14(8)	C(7)	0.1506(5)	0.4306(9)	0.5661(6)	4.22(25)
C(8)	0.2197(2)	0.5183(3)	0.5539(2)	3.14(6)	C(8)	0.2187(4)	0.4993(9)	0.5523(5)	3.22(21)
C(9)	0.3535(2)	1.0612(4)	0.6205(2)	4.16(8)	C(9)	0.3591(5)	1.0259(10)	0.6198(5)	4.11(23)
C(10)	0.4243(2)	1.0112(4)	0.6017(2)	4.43(9)	C(10)	0.4276(5)	0.9738(10)	0.5979(5)	3.97(23)
C(11)	0.4404(2)	0.8461(4)	0.5868(2)	3.89(8)	C(11)	0.4391(4)	0.8083(10)	0.5818(5)	3.76(22)
C(12)	0.3843(2)	0.7242(4)	0.5870(2)	3.23(7)	C(12)	0.3817(4)	0.6946(9)	0.5840(5)	3.17(20)
C(21)	0.2187(1)	0.4540(3)	0.3541(2)	2.90(6)	C(21)	0.2146(4)	0.4590(9)	0.3408(5)	3.23(20)
C(22)	0.1522(2)	0.5423(4)	0.3416(2)	3.65(7)	C(22)	0.1515(4)	0.5537(10)	0.3361(5)	4.04(24)
C(23)	0.1147(2)	0.5604(5)	0.2478(3)	4.65(9)	C(23)	0.1122(5)	0.5928(12)	0.2461(6)	5.14(28)
C(24)	0.1431(2)	0.4904(5)	0.1663(2)	5.14(10)	C(24)	0.1358(5)	0.5321(12)	0.1614(6)	4.82(26)
C(25)	0.2098(2)	0.4055(5)	0.1786(2)	5.28(11)	C(25)	0.1967(6)	0.4406(13)	0.1647(6)	5.80(32)
C(26)	0.2480(2)	0.3850(4)	0.2719(2)	4.26(9)	C(26)	0.2381(5)	0.4001(12)	0.2539(6)	5.16(28)
C(31)	0.4788(1)	0.5247(3)	0.7060(2)	3.07(6)	C(31)	0.4829(4)	0.4948(8)	0.7146(5)	3.05(20)
C(32)	0.4639(2)	0.6197(4)	0.7881(2)	3.49(7)	C(32)	0.4656(4)	0.5943(9)	0.7913(5)	3.60(21)
C(33)	0.5121(2)	0.6102(4)	0.8750(2)	4.46(9)	C(33)	0.5146(6)	0.6012(12)	0.8780(6)	5.31(29)
C(34)	0.5744(2)	0.5076(5)	0.8803(3)	5.26(10)	C(34)	0.5780(6)	0.5082(12)	0.8880(7)	6.08(33)
C(35)	0.5891(2)	0.4152(5)	0.7996(3)	5.52(11)	C(35)	0.5944(6)	0.4087(13)	0.8119(8)	6.94(36)
C(36)	0.5418(2)	0.4249(4)	0.7109(3)	4.07(8)	C(36)	0.5466(5)	0.4034(11)	0.7232(7)	5.26(29)

a) $B_{eq}=4/3\sum_i\sum_j \beta_{ij}\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

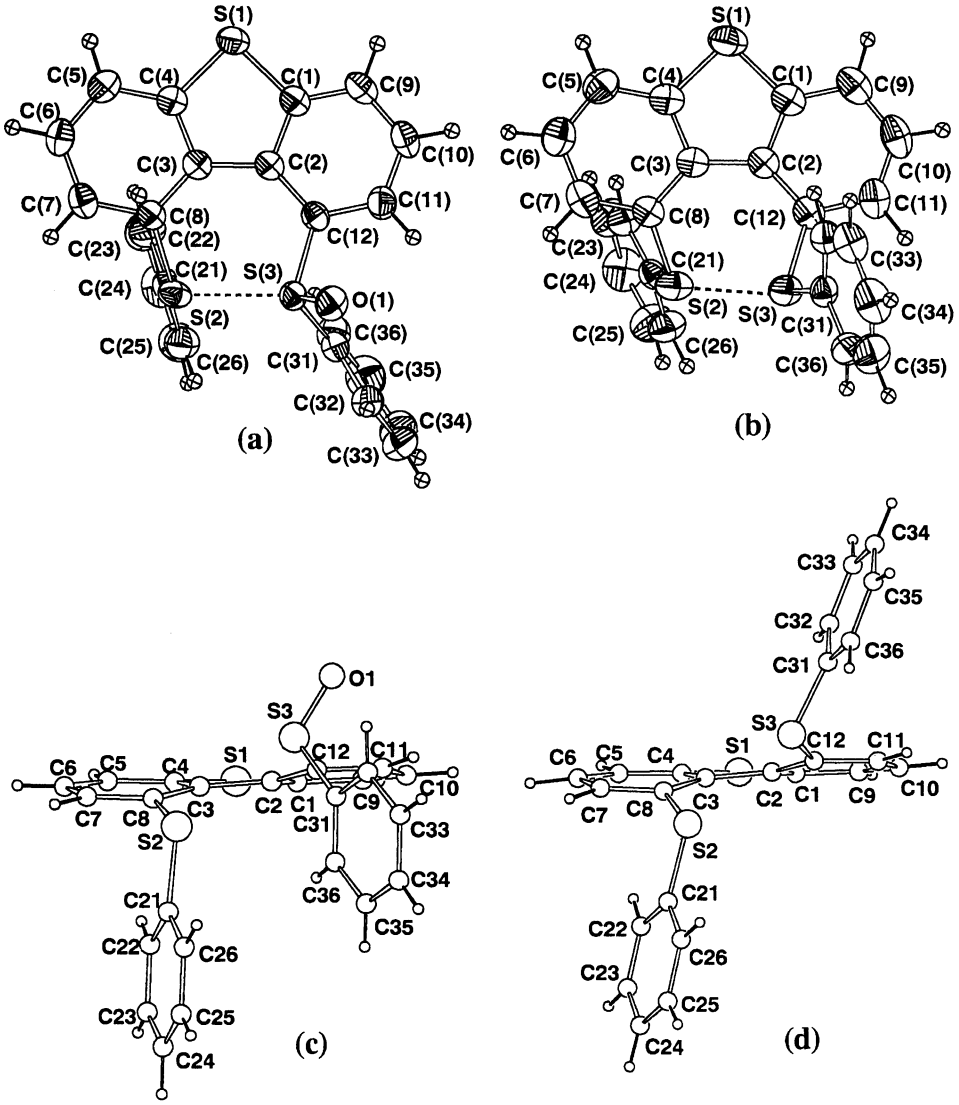
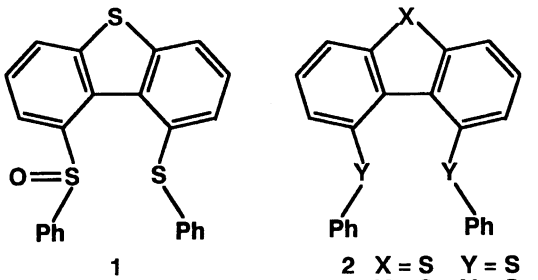


Fig. 1. ORTEP drawings with the atom-numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability and the H atoms are drawn as spheres with a radius of 0.1 Å. (**a**) **1** and (**b**) **2**. Projections of the molecules viewed along the thiophene planes. (**c**) **1** and (**d**) **2**.



Scheme 1.

munications using the programs UNICS III,[13] MULTAN78, and ORTEP II.[14]

Discussion

The molecular structures of **1** and **2** with the atomic numbering scheme are shown in Fig. 1. The molecular structures of **3** and **4** are similar to that of **2**. Selected bond distances and angles are listed in Table 3. Some torsion angles are listed in Table 4 along with those obtained by energy calculations.

Structure of 1. The planarity of the thiophene ring is slightly distorted as a half-chair form with the maximum deviation of 0.046(5) Å. It is clear from the figure and from measures of planarity that the phenylthio and phenylsulfinyl groups cause a significant deformation of the dibenzothiophene moiety. The phenylsulfinyl group is forced out of plane on one side of the plane, and the phenylthio group on the opposite side of the plane. The torsion angles of C(12)–C(2)–C(3)–C(8), C(2)–C(3)–C(8)–S(2), and C(3)–C(2)–C(12)–S(3) are −19.1(2), −12.6(2), and −16.5(2)°, respectively. The deviations of the S(2) and S(3) atoms from the plane of the thiophene ring are 0.810(3) and −0.980(3) Å, re-

Table 3. Selected Bond Lengths (l) and Angles (θ).

	1 l/Å	**2** l/Å	**3** l/Å	**4** l/Å
S(1)–C(1)	1.744(2)	1.744(3)	1.875(4)[a]	1.875(8)[a]
S(1)–C(4)	1.742(2)	1.746(3)	1.897(4)[a]	1.899(8)[a]
S(2)–C(8)	1.776(2)	1.776(3)	1.780(4)	1.922(7)[a]
S(2)–C(21)	1.778(2)	1.781(3)	1.782(4)	1.914(7)[a]
S(3)–O(1)	1.498(1)			
S(3)–C(12)	1.810(2)	1.786(3)	1.778(4)	1.936(7)[a]
S(3)–C(31)	1.812(2)	1.783(3)	1.783(4)	1.933(7)[a]
C(1)–C(2)	1.415(2)	1.417(4)	1.399(5)	1.427(10)
C(1)–C(9)	1.386(3)	1.395(5)	1.404(6)	1.377(12)
C(2)–C(3)	1.461(2)	1.456(4)	1.470(6)	1.455(10)
C(2)–C(12)	1.411(2)	1.413(4)	1.420(6)	1.404(11)
C(3)–C(4)	1.401(2)	1.414(4)	1.407(6)	1.408(11)
C(3)–C(8)	1.412(2)	1.411(4)	1.399(5)	1.422(10)
C(4)–C(5)	1.394(2)	1.394(5)	1.382(7)	1.380(11)
C(5)–C(6)	1.370(3)	1.377(5)	1.368(7)	1.364(12)
C(6)–C(7)	1.388(3)	1.395(5)	1.402(7)	1.410(13)
C(7)–C(8)	1.386(2)	1.389(4)	1.390(7)	1.386(12)
C(9)–C(10)	1.368(3)	1.374(5)	1.382(7)	1.374(12)
C(10)–C(11)	1.386(3)	1.379(5)	1.385(6)	1.387(12)
C(11)–C(12)	1.379(2)	1.402(4)	1.398(6)	1.395(11)
	θ/°	θ/°	θ/°	θ/°
C(1)–S(1)–C(4)	90.7(1)	91.3(1)	86.6(2)[a]	87.1(3)[a]
C(8)–S(2)–C(21)	102.7(1)	101.5(1)	101.5(2)	98.8(3)[a]
O(1)–S(3)–C(12)	105.4(1)			
O(1)–S(3)–C(31)	104.9(1)			
C(12)–S(3)–C(31)	98.1(1)	100.1(1)	99.9(2)	97.6(3)[a]
S(1)–C(1)–C(2)	113.0(1)	112.7(2)	113.5(3)[a]	112.7(5)[a]
S(1)–C(1)–C(9)	124.3(1)	124.0(2)	123.0(3)[a]	123.7(6)[a]
C(2)–C(1)–C(9)	122.5(2)	123.2(3)	123.3(4)	123.4(7)
C(1)–C(2)–C(3)	111.0(1)	111.2(2)	113.3(4)	113.0(6)
C(1)–C(2)–C(12)	116.1(2)	116.3(3)	116.6(4)	115.0(7)
C(3)–C(2)–C(12)	132.6(2)	132.2(3)	129.8(4)	131.8(7)
C(2)–C(3)–C(4)	111.2(2)	111.4(2)	113.2(4)	114.1(6)
C(2)–C(3)–C(8)	132.1(2)	131.7(3)	130.2(4)	130.6(7)
C(4)–C(3)–C(8)	116.6(2)	116.7(3)	116.4(4)	115.1(7)
S(1)–C(4)–C(3)	113.5(1)	112.6(2)	112.5(3)[a]	112.1(5)[a]
S(1)–C(4)–C(5)	123.3(1)	124.5(2)	123.9(4)[a]	123.8(6)[a]
C(3)–C(4)–C(5)	123.1(2)	122.8(3)	123.4(4)	123.9(7)
C(4)–C(5)–C(6)	118.3(2)	118.6(3)	118.6(5)	119.5(8)
C(5)–C(6)–C(7)	120.2(2)	119.7(3)	119.6(5)	119.3(8)
C(6)–C(7)–C(8)	121.5(2)	121.8(3)	121.3(5)	120.8(8)
S(2)–C(8)–C(3)	122.6(1)	121.7(2)	122.2(3)	122.4(6)[a]
S(2)–C(8)–C(7)	117.3(1)	118.1(2)	117.4(4)	116.1(6)[a]
C(3)–C(8)–C(7)	119.6(2)	119.4(3)	119.6(4)	120.6(7)
C(1)–C(9)–C(10)	119.1(2)	117.9(3)	118.1(4)	119.4(8)
C(9)–C(10)–C(11)	120.0(2)	121.2(3)	120.0(5)	119.4(8)
C(10)–C(11)–C(12)	121.2(2)	121.0(3)	121.8(4)	121.2(8)
S(3)–C(12)–C(2)	123.1(1)	122.8(2)	123.8(3)	123.8(6)[a]
S(3)–C(12)–C(11)	114.8(1)	116.8(2)	116.2(3)	114.3(6)[a]
C(2)–C(12)–C(11)	120.4(2)	119.7(3)	119.2(4)	120.8(7)
S(2)–C(21)–C(22)	125.5(1)	126.0(2)	125.8(3)	125.5(6)[a]
S(2)–C(21)–C(26)	115.3(1)	114.3(2)	113.9(3)	115.4(6)[a]
S(3)–C(31)–C(32)	116.5(2)	122.4(2)	122.6(3)	121.2(6)[a]
S(3)–C(31)–C(36)	122.7(2)	117.4(2)	117.0(3)	117.8(6)[a]

a) S means Se.

spectively. Despite these deviations, the S···S distance (3.016(1) Å) is shorter than the van der Waals contact (82.0% of the van der Waals contact).

It can be clearly seen from the figure and the torsion angles that the configurations about the two phenylthio groups are different, so that O(1) is just on the opposite side of the phenyl group (C(31)—C(36)) from the thiophene plane. The phenyl group (C(21)—C(26)) is on the same side of C(31)—C(36). Considering the axial chirality, the molecular configuration depicted in Fig. 1 is aS, R_S. Therefore, the molecular configuration in the crystals of **1** is aS, R_S/aR, S_S. The existence of the diastereomer, aS, S_S/aR, R_S, couldn't be observed before and after recrystallization.

In crystals there are no significant intermolecular interactions, except for the van der Waals interaction.

Structures of 2, 3, and 4. Slight distortions of the thiophene or selenophene rings are similar to that of **1**. The maximum deviations from the ring-plane are 0.045(3), 0.050(3) and 0.050(5) Å, for **2**, **3**, and **4**, respectively. The conformations of the phenylthio/seleno groups about S/Se are different from those of **1**. In **2**, **3**, and **4**, the phenyl group (C(31)—C(36)) is at the same position of the O(1) atom of **1**, so that two phenyl groups (C(21)—C(26) and C(31)—C(36)) are on opposite sides from each other. Phenylthio or phenylseleno groups also cause a significant deformation of the dibenzothio/selenophene moieties. The C(12)–C(2)–C(3)–C(8) torsion angles are −20.7(4), −22.6(5), and −20.4(9)°, for **2**, **3**, and **4**, respectively. The deviations of the S(2) and S(3) atoms from the plane of the thio/selenophene ring are 0.982(4) and −0.917(4) Å for **2**, 1.005(6) and −1.000(6) Å for **3**, and 1.025(10) and −1.074(10) Å for **4**.

In spite of a distortion of the dibenzothio/selenophene moiety, the S···S (3.012(1) and 2.973(1) Å for **2** and **3**, respectively) and Se···Se (3.070(1) Å for **4**) distances are shorter than the van der Waals contacts and shorter than the transannular S···S contacts (3.121—3.271 Å) of 1-thionia-5-thiacyclooctane salts and 1,5-dithiacyclooctanes. The shortest S···S distance of a horseshoe-like S–C_4–S moiety, searched from Cambridge Structural Database (CSD),[15] is 3.103 Å of tetrakis(1,3-dithiol-2-ylidene)cyclobutane.[16] The S···S contacts (2.973—3.016 Å) in the present molecules are the shortest case found so far. In σ-sulfuranes and 1,5-dithiacyclooctanes, an addition of the electronegative group to a sulfur atom has reduced the S···X distance. However, no such shortening of the S···S distance was observed for the case of **1**, compared with **2**.

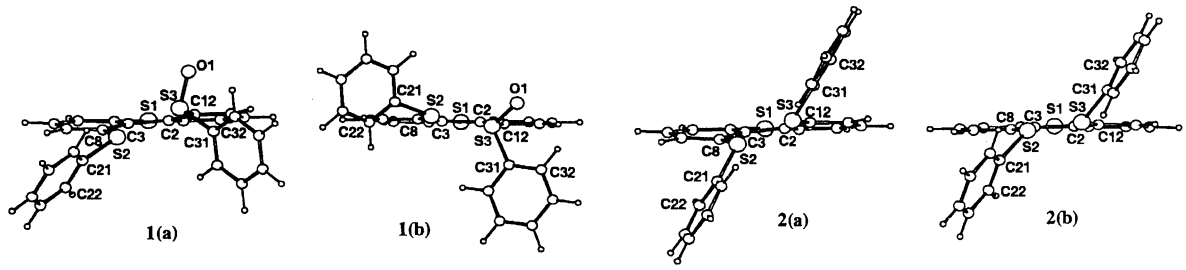
Crystals of **2**—**4** are isostructures of each other, with no significant intermolecular interactions, except for the van der Waals interaction.

Comparison of the Dibenzothio/selenophene Moieties. Selected dimensions of the dibenzothio/selenophene moieties of unsubstituted dibenzothiophenes[17,18] and dibenzoselenophene[19] and some 1,9-

Table 4. S···S or Se···Se Distances (l/Å), Selected Torsion Angles (τ/°) of Observed and Optimized Molecules with Energy Differences (ΔE/kJ mol^{-1})

	Observed molecules				Calculated molecules			
	1	**2**	**3**	**4**[a)]	**1(a)**	**1(b)**	**2(a)**	**2(b)**
S(2)···S(3)	3.016(1)	3.012(1)	2.973(1)	3.070(1)	2.550	2.376	2.219	2.042
C(12)–C(2)–C(3)–C(8)	−19.1(2)	−20.7(4)	−22.6(5)	−20.4(9)	−19.1	7.1	−20.7	−5.2
C(3)–C(2)–C(12)–S(3)	−16.5(2)	−13.6(3)	−14.0(5)	−16.8(9)	−0.9	1.0	4.9	−1.9
C(2)–C(3)–C(8)–S(2)	−12.6(2)	−16.6(3)	−16.7(5)	−17.0(8)	−1.9	0.5	3.3	0.7
C(3)–C(8)–S(2)–C(21)	−94.3(1)	−101.0(2)	−99.8(3)	−95.6(5)	−155.3	162.7	−133.3	−140.0
C(8)–S(2)–C(21)–C(22)	1.7(1)	0.6(2)	0.4(3)	−1.7(6)	45.4	84.7	14.9	41.1
C(2)–C(12)–S(3)–O(1)	−121.2(1)				−111.8	−136.5		
C(2)–C(12)–S(3)–C(31)	130.8(1)	−115.9(2)	−115.1(3)	−113.5(5)	139.0	115.4	−135.6	−133.7
C(12)–S(3)–C(31)–C(32)	138.9(1)	39.7(1)	41.3(3)	40.1(5)	123.9	97.6	18.2	32.7
ΔE/kJ mol^{-1} [b)]					−40.7	−57.4	−41.7	−61.9

a) S means Se. b) Energy difference between observed molecule in which only H atoms are optimized and optimized molecule. **1(a)**, **2(a)**: Partially optimized molecules (retaining distorted dibenzothiophenes) for **1** and **2**, respectively. **1(b)**, **2(b)**: Fully optimized molecules for **1** and **2**, respectively (See Scheme 2).



Scheme 2.

disubstituted derivatives searched from CSD are listed in Table 5. For unsubstituted compounds and octafluorodibenzothiophene[20] the moieties are planar because of a nonsteric hindrance between the 1,9-positions, while substituted compounds with bulky groups[21,22] show a large distortion of the moieties. No differences in the bond lengths and angles of the thiophene or selenophene rings were observed between planar and distorted molecules. On the other hand, the dimensions of the benzene rings of the dibenzothio/selenophene moieties of substituted compounds deform from a regular hexagon. The angles C(2)–C(1)–C(9) and C(3)–C(4)–C(5) (δ) are larger and C(1)–C(2)–C(12) and C(4)–C(3)–C(8) (ε) are smaller than 120°. The lengths of C(2)–C(12) and C(3)–C(8) (**e**) of distorted compounds are longer than those of planar compounds.

Energy Calculations. In order to investigate the conformation of the substituents and the planarity of dibenzothiophenes, simple energy calculations were carried out with semi-empirical molecular-orbital calculations using CNDO/2 and PM3 methods.[23] As mentioned above, two phenyl groups of **1** are on the same side from the dibenzothiophene moiety, while those of **2**—**4** are on the opposite sides. For three models of **1**, the energy changes as a torsion angle of C(12)–S(3)–C(31)–C(32) (ω) were calculated by CNDO/2, as shown in Fig. 2. A graph (**a**) shows an energy change of a model with torsion angles ϕ (C(2)–C(12)–S(3)–O(1)) = −121.2° and φ (C(2)–C(12)–S(3)–C(31)) = 130.8° (observed conformation with aS, R_S configura-

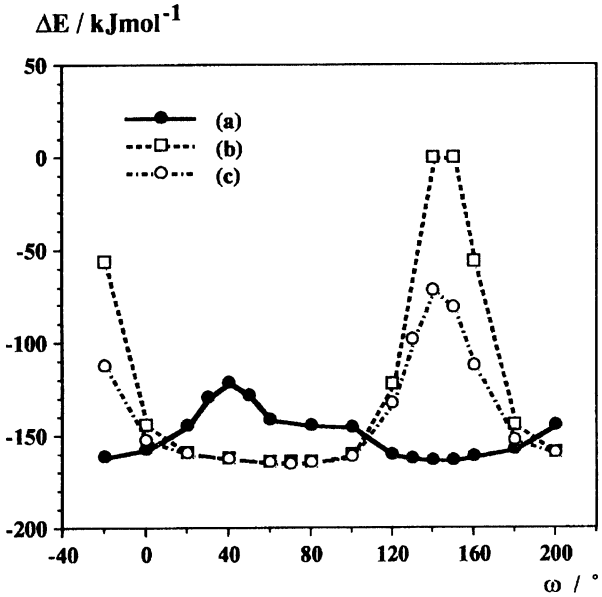
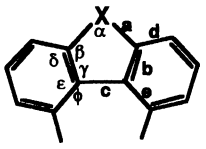


Fig. 2. Energy changes of the molecule **1** as a torsion angle of C(12)–S(3)–C(31)–C(32) (ω) calculated by CNDO/2. (**a**) A model with the observed configuration (aS, R_S) at S(3). (**b**) Inverse configuration (aS, S_S) of **1**. (**c**) Same conformation as **2** with inverse configuration (aS, S_S) of **1**.

Table 5. Comparison of the Geometry between Distorted and Planar Dibenzothio/selenophenes

	1	**2**	SAKJOD	CIGLAF	DBZTHP	DBTTNB	SANXAG	**3**	**4**	SAKJUJ	DBZSEL
τ/°	19.1	20.7	21.2	20.0	0.9	0.3	0.2	22.6	20.4	20.3	0.9
θ/°	13.5	14.4	16.4	15.6	1.3	2.0	0.0	16.0	14.5	18.4	1.7
a/Å	1.743	1.745	1.745	1.736	1.740	1.747	1.737	1.886	1.887	1.891	1.890
b/Å	1.408	1.416	1.407	1.407	1.408	1.395	1.404	1.404	1.418	1.409	1.391
c/Å	1.461	1.456	1.478	1.456	1.442	1.453	1.470	1.470	1.455	1.456	1.448
d/Å	1.390	1.395	1.376	1.408	1.386	1.394	1.395	1.393	1.379	1.378	1.392
e/Å	1.412	1.412	1.423	1.435	1.391	1.391	1.395	1.410	1.413	1.443	1.392
α/°	90.7	91.3	91.5	91.2	91.5	91.2	89.8	86.6	87.1	87.1	86.7
β/°	113.3	112.7	112.7	112.9	112.3	112.5	114.6	113.0	112.4	111.9	112.3
γ/°	111.1	113.3	111.1	111.2	111.9	111.9	110.5	113.3	113.6	113.7	114.3
δ/°	122.8	123.0	123.7	122.9	121.6	121.6	120.7	123.4	123.7	125.1	121.5
ε/°	116.4	116.5	116.9	117.4	118.7	119.1	118.1	116.5	115.1	115.1	118.1
ϕ/°	132.4	132.0	132.0	131.3	129.3	129.0	131.5	130.0	131.2	131.7	127.6



τ torsion angle e-c-e'
θ dihedral angle between benzene rings

Ref. code in CSD.
SAKJOD: 1,9-bis(dimethylamino)dibenzothiophene.[21]
CIGLAF: thieno[3,2-*e*:4,5-*e'*]bis[1](benzothiophene).[22]
DBZTHP: dibenzothiophene.[17]
DBTTNB: dibenzothiophene-trinitrobenzene complex.[18]
SANXAG: octafluorodibenzothiophene.[20]
SAKJUJ: 1,9-bis(dimethylamino)dibenzoselenophene.[21]
DBZSEL: dibenzoselenophene.[19]

tion). The torsion angle (ω=140°) with the minimum energy is compared to the observed value of 138.9°. A model of **1** with opposite phenyl groups has a diastereomeric configuration, a*S*, *S*S; (**b**) and (**c**) show energy changes of models of diastereomeric configuration, a*S*, *S*S, with ϕ=130.8° and φ=−121.2° (just inverse on S atom of **1**) and with ϕ=136.1° and φ=−115.9° (same torsion angle, φ, as **2**), respectively. The calculated energies of these models for ω=140° are very high because of a steric interaction between the H atom of the phenyl group and the dibenzothiophene ring. The minimum values were obtained at about ω=70°, where calculated energies are slightly smaller than that of the observed model (**a**). This suggests that the observed configuration of **1** may not be intrinsic in the molecule, itself, although only a*S*, *R*S/a*R*, *S*S configurations were obtained. An intermolecular interaction takes part in the molecular configuration because an axial configuration may not be retained in solution.

Starting from the observed molecules of **1** and **2**, the minimum energy was searched while optimizing all of the atoms by the PM3 method. For both **1** and **2** the calculated molecules (**1(b)** and **2(b)** in Scheme 2) have planar dibenzothiophenes with very short S···S contacts (2.376 and 2.042 Å for **1** and **2**, respectively). Calculations with the models fixing distorted dibenzothiophene moieties (partially optimized) also show short S···S contacts (2.550 and 2.219 Å for **1** and **2**, respectively, **1(a)** and **2(a)** in Scheme 2). The energy differences between the observed and optimized molecules and the selected torsion angles of these optimizing molecules are also listed in Table 4. Shortening of the S···S contacts is mainly caused by a flattening of the torsion angles, C(2)–C(3)–C(8)–S(2) and C(3)–C(2)–C(12)–S(3). Optimization of the molecules changed these values to 0.5—5° from the observed torsion angles of 12—17°. In the observed molecules, the S(2) and S(3) atoms deviate from the benzene rings by about 0.5 Å. These results suggest that an approximate energy calculation used here could not estimate the distortion of the molecular moiety correctly; that is, the distortion energy may be overestimated and/or the S···S steric repulsion may be underestimated in these calculations. Viewed from a different point, these results suggest that molecules **1** and **2**, of which crystals are very stable in air, would be easily converted to disulfides. In fact, ring disulfides were obtained by the thermolysis of the bis(methylthio) derivative.[8]

A preliminary study of a deformation electron-densities of **2** obtained by a low-temperature X-ray diffraction method suggests that the lobes of the lone-pair electrons of two sulfide groups are just perpendicular to the C–S–C_{Ph} planes and orthonormal with each other so as to avoid a steric hindrance between the lone pairs of two S atoms.[24] In the flatmolecule, the lobes of lone pairs should be parallel to each other.

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