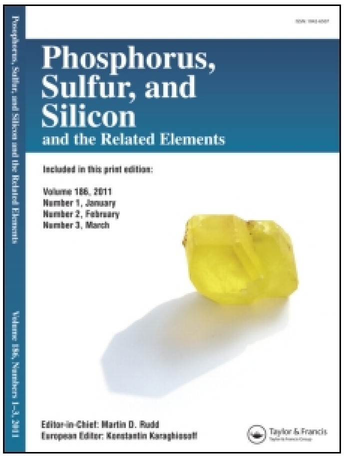


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

CRYSTAL AND MOLECULAR STRUCTURE OF N,N'-DIMETHYL-2,2'-DISELENODIBENZOAMIDE AND N,N'-DIPHENYL-2,2'-DISELENODIBENZOAMIDE

Malgorzata Piqtek[a]; Ewa Zeslawska[b]
[a] Faculty of Chemistry, Jagiellonian University, Kraków, Poland [b] Department of Chemistry, Pedagogical University, Kraków, Poland

To cite this Article Piqtek, Malgorzata and Zeslawska, Ewa(1996) 'CRYSTAL AND MOLECULAR STRUCTURE OF N,N'-DIMETHYL-2,2'-DISELENODIBENZOAMIDE AND N,N'-DIPHENYL-2,2'-DISELENODIBENZOAMIDE', Phosphorus, Sulfur, and Silicon and the Related Elements, 117: 1, 55 — 65

To link to this Article: DOI: 10.1080/10426509608038774

URL: http://dx.doi.org/10.1080/10426509608038774

Phosphorus, Sulfur, and Silicon, 1996, Vol. 117, pp. 55–65
Reprints available directly from the publisher
Photocopying permitted by license only

CRYSTAL AND MOLECULAR STRUCTURE OF N,N′-DIMETHYL-2,2′-DISELENODIBENZOAMIDE AND N,N′-DIPHENYL-2,2′-DISELENODIBENZOAMIDE

MAŁGORZATA PIĄTEK[a,*] and EWA ŻESŁAWSKA[b]

[a]*Faculty of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060 Kraków, Poland;* [b]*Department of Chemistry, Pedagogical University, ul. Podchorążych 2, 30-084 Kraków, Poland*

(Received 19 March 1996; In final form 30 April 1996)

The crystal structure of N,N′-dimethyl-2,2′-diselenodibenzoamide (DMBS) and N,N′-diphenyl-2,2′-diselenodibenzoamide (DEBS) has been determined with the use of X-ray diffraction method. The molecular structures of DMBS and DEBS are very similar. The molecules have twofold symmetry with the crystallographic 2 axis perpendicular to Se-Se bond. The absolute values of C-Se-Se-C torsion angles are 82.4(2)° and 86.1(4)° in DMBS and DEBS, respectively. Intramolecular Se···O short contacts of 2.849(8)A in DEBS and 2.742(5)A in DMBS were observed. The *trans*-amide moieties form intermolecular hydrogen bonds leading to ribbon-like arrangement of the molecules in both structures. The influence of a substituent at N atom manifests itself in packing difference between DMBS and DEBS crystalline structures. A comparison of molecular geometry and packing of studied diselenides with the sulfur analogue of DMBS has been performed.

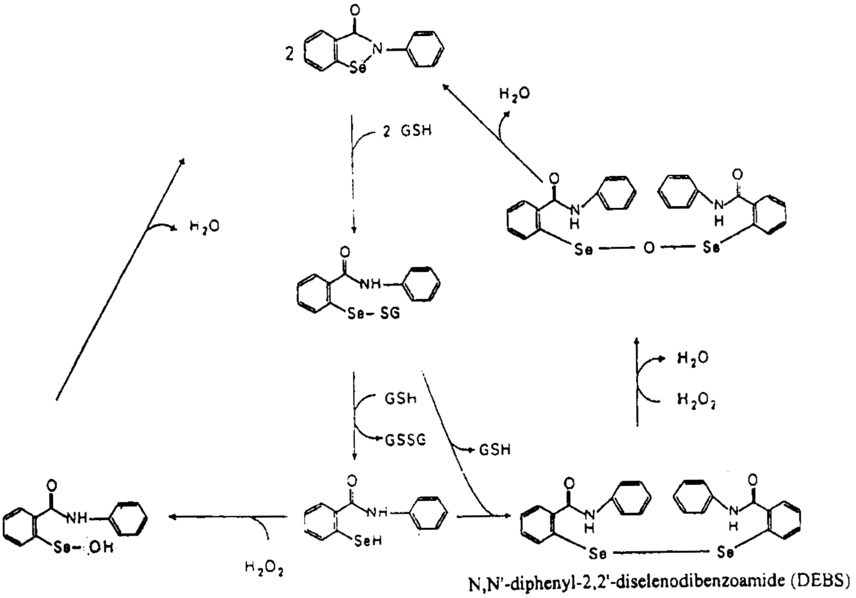
Keywords: Diselenides; crystal structure; Selenium hypervalency; hydrogen bonding

INTRODUCTION

The title compounds may be formed in a natural way during the reaction cycle of catalytic reduction of H_2O_2 with 2-phenyl-1,2-benzisoselenazol-3(2H)one (ebselen) and its methyl derivative[1]. The mechanism of this reduction suggested by Haenen and modified by Morgenstern[2]. (Scheme 1) is very similar to that characteristic of the enzyme glutathione peroxidase (GSH-Px)[3]. This selenoen-

---

[*] Corresponding author.



SCHEME 1 The simplified mechanism of H_2O_2 reduction by 2-phenyl-1,2-benzisoselenazol-3(2H)- -one suggested by Haenen[1]and modified by Morgenstern[2].

zyme is one of the major factors responsible for antioxidant defense in living organisms. According to the mechanism proposed by Haenen, diselenides are produced as a result of the reaction between the selenol form of the substrate compound (ebselen or its methyl derivative) and mixed selenosulfide (complex of benzisoselenazolone with glutathione) formed in one of the former stages of this cycle. Diselenide is capable of direct reaction with hydroperoxide which is an important stage for this catalytic degradation of H_2O_2.

This work is a fragment of our studies on the relationship between the molecular structure and biological activity of selected benzisoselenazolones. The aim of the X-ray structure analysis of N,N′-dimethyl-2,2′-diselenodibenzoamide (DMBS) and N,N′-diphenyl-2,2′-diselenodibenzoamide (DEBS) was to determine the influence of a substituent at N atom on the molecular structures of studied diselenides as well as comparison with the known structure of sulfur analogue of DMBS, N,N′-dimethyl-2,2′-dithiodibenzoamide (DMBT) reported by Iwasaki *et al.*[5]. This comparison could help us to understand the effect of the chalcogen atom kind on the molecular geometry of the investigated compounds.

EXPERIMENTAL

Crystals of N,N'-Dimethyl-2,2'-diselenodibenzoamide (DMBS) and N,N'-Diphenyl-2,2'-diselenodibenzoamide (DEBS) were kind gifts from Prof. A. Inglot (Laboratory of Virology, Institute of Immunology and Experimental Therapy, Polish Academy of Sciences, Wrocław, Poland) and Prof. J. Młochowski (Institute of Organic and Physical Chemistry, Technical University, Wrocław, Poland), respectively. Data collection: CAD-4 for DEBS and KM-4 for DMBS, cell refinement CAD-4 diffractometer software for DEBS and KM-4 diffractometer software for DMBS. Program used to solve structures: SHELXS86[9], Program used to refine structures: SHELXL93[10], geometrical calculations and drawings: PARST95[11], ORTEP[12]. All computations were performed on PC486 computer. Details of data collection and structure refinement are shown in Table I. The final atomic parameters are given in Table II.

DISCUSSION

The molecular structures of DMBS and DEBS with the atomic numbering are shown in Fig. 1 and Fig. 2. Bond distances, bond angles and selected torsion angles are listed in Table III, IV, V. Molecular packings of DMBS and DEBS are depicted in Fig. 3 and 4.

The analysis of the geometry of N,N'-dimethyl-2,2'-diselenodibenzoamide (DMBS) and N,N'-diphenyl-2,2'-diselenodibenzoamide (DEBS) has shown close similarity of their bond lengths. The only differences worth mentioning concern the bonds Se-Se and Se-C_{ar}. The length of Se-Se bond is slightly longer in DMBS (2.334(1)Å), than in DMBS (2.317(2)Å), while the standard value of this kind of bond is 2.340(24)Å[4]. The bonds of type C_{ar}-Se are longer than their standard value, i.e. 1.930(6)Å[4], namely their lengths are 1.951(10)Å in DEBS and 1.948(6)Å in DMBS. The remaining bond lengths in both studied diselenides are comparable to the standard ones[4], also the analogous bond lengths are comparable to each other. Even the lengths of bonds N-substituent ($-CH_3$ in DMBS and $-C_6H_5$ in DEBS) remain comparable within 3σ limitation.

The values of bond angles in DEBS are also close to the corresponding ones in DMBS. The surroundings of the nitrogens in both diselenides are planar within 3σ range indicating the sp^2 hybridization of these atoms. The amide hydrogen atoms adopt the antiperiplanar orientation in the -C-O-N-H skeleton. The benzene moieties in the two structures are approximately planar with much larger deviations from planarity observed in DMBS. In both molecules each selenium atom

TABLE I Details of data collection and structure refinement for structures of N,N'-dimethyl-2,2'-diselenodibenzoamide (DMBS) and N,N'-diphenyl-2,2'-diselenodibenzoamide (DEBS)

	DMBS	*DEBS*
Chemical formula	$C_{16}H_{16}Se_2O_2N_2$	$C_{26}H_{20}Se_2O_2N_2$
Mw	426.23	550.376
Crystal habit	pale yellow plates	colourless prisms
Crystal system	monoclinic	monoclinic
Space group	C 2/C	C 2/C
a(Å)	18.294(5)	24.350(6)
b(Å)	9.606(4)	5.039(1)
c(Å)	9.422(2)	19.186(6)
β(deg)	94.07(4)	109.59(2)
V(Å^3)	1652(1)	2218(1)
Z	4.0	4.0
Dc(g cm^{-3})	1.714	1.6483
F(000)	840.0	1096.0
Radiation (Å)	MoKα, λ = 0.71093	CuKα, λ = 1.54178
µ(MoKα) (cm^{-1})	4.485	4.383
Diffractometer	KM-4	CAD-4
Monochromator	graphite	graphite
Data collection range (deg)	2.23 to 30.08	3.00 to 52.00
Scan width	1.0 + 0.35 tgΘ	1.1 + 0.14 tgΘ
Scan mode	ω/2Θ	ω/2Θ
Range of hkl h	−25 to 25	0 to 5
k	0 to 13	−12 to 12
l	−13 to 13	−18 to 18
No. of reflections measured	3738	1978
No. of reflections unique	2159	1060
No. of reflections observed	1260 I > 2sigma(I)	887 I > 2sigma(I)
wR	0.1358	0.1123
R	0.0665	0.0424
S	1.154	0.959
Max shift/(esd)	0.021	0.001
Peaks in final map (eÅ^{-3})	max 1.367, min −0.659	max 0.595, min −0.489

is approximately coplanar with the benzene ring to which it is linked. The phenyl substituents in DEBS show slightly greater deviations from planarity than the benzene fragments of this structure but they still remain planar.

The analysis of the torsion angles in DMBS and DEBS provided the evidence that both molecules have very similar conformations. Both molecules have two-fold symmetry with the crystallographic 2 axis perpendicular to Se-Se bond. The two mutually symmetrical halves of each molecule are twisted, so that the absolute values of C-Se-Se-C torsion angles are 82.4(2)° and 86.1(4)° in DMBS and DEBS, respectively. The differences between the other analogous torsion angles in the two diselenides do not exceed 10°. Certain difference in the overall shape of the two molecules may be noticed in the angles between the planes of

TABLE II Fractional atomic coordinates and equivalent isotropic displacement parameters (A^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i\, a_j{}^*\mathrm{a}_i\mathrm{a}_j$.

(a) N,N'-Dimethyl-2,2'-diselenodibenzoamide (DMBS):

Atom	X/a	Y/b	Z/c	Ueq
Se1	0.06395(3)	0.05396(6)	0.25733(7)	600(2)
C1	0.0848(3)	0.2034(6)	0.1264(6)	477(17)
C2	0.0309(3)	0.2533(9)	0.0293(7)	670(27)
C3	0.0462(4)	0.3634(9)	−0.0614(7)	781(28)
C4	0.1138(4)	0.4156(8)	−0.0592(7)	671(28)
C5	0.1685(3)	0.3688(6)	0.0360(6)	525(20)
C6	0.1549(3)	0.2618(5)	0.1310(5)	432(16)
C7	0.2133(2)	0.2075(5)	0.2326(6)	436(17)
C8	0.3254(4)	0.2553(8)	0.3786(9)	593(23)
O1	0.2132(2)	0.0859(4)	0.2717(5)	603(15)
N1	0.2650(2)	0.2960(5)	0.2826(5)	488(15)

(b) N,N'-Diphenyl-2,2'-diselenodibenzoamide (DEBS):

Atom	X/a	Y/b	Z/c	Ueq
Se1	0.04886(4)	0.09429(21)	0.28599(6)	335(6)
C1	0.0524(4)	0.3703(19)	0.3586(51)	275(43)
C2	0.0023(5)	0.4550(24)	0.3719(69)	390(47)
C3	0.0068(5)	0.6460(23)	0.4239(63)	399(46)
C4	0.0585(5)	0.7558(25)	0.4629(68)	434(53)
C5	0.1084(5)	0.6756(22)	0.4508(61)	323(44)
C6	0.1060(4)	0.4826(19)	0.3979(54)	242(40)
C7	0.1595(4)	0.3837(23)	0.3852(55)	309(44)
C8	0.2522(4)	0.5455(21)	0.3734(59)	309(46)
C9	0.2894(5)	0.3394(22)	0.4078(67)	373(52)
C10	0.3409(5)	0.3092(27)	0.3938(78)	464(51)
C11	0.3559(5)	0.4785(26)	0.3465(69)	428(54)
C12	0.3195(5)	0.6831(25)	0.3141(70)	452(53)
C13	0.2685(6)	0.7139(27)	0.3276(73)	420(52)
N1	0.1980(3)	0.5842(16)	0.3860(41)	512(32)
O1	0.1682(4)	0.1562(18)	0.3743(57)	236(42)

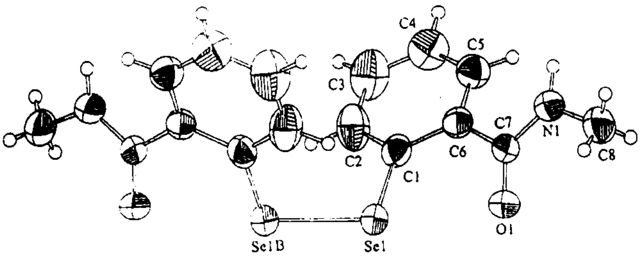


FIGURE 1 The molecular structure of DMBS with atomic numbering for non-H atoms. The thermal elipsoids for non-H atoms are drawn at 30% probability.

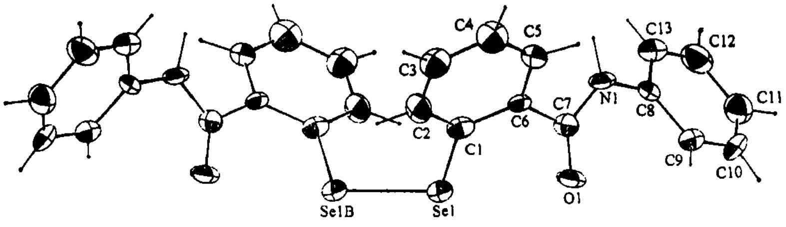


FIGURE 2 The molecular structure of DEBS with atomic numbering for non-H atoms. The thermal elipsoids for non-H atoms are drawn at 30% probability.

TABLE III Bond distances (Å)

(a) N,N'-Dimethyl-2,2'-diselenodibenzoamide (DMBS)	
Se1-C1	1.948(6)
Se1-Se1B	2.334(1)
C1-C2	1.383(8)
C2-C3	1.400(11)
C4-C3	1.332(10)
C5-C4	1.372(9)
C6-C5	1.397(8)
C7-C6	1.479(7)
C6-C1	1.397(7)
O1-C7	1.225(6)
N1-C7	1.332(7)
N1-C8	1.431(9)
(b) N,N'-Diphenyl-2,2'-diselenodibenzoamide (DEBS)	
Se1-C1	1.950(10)
Se1-Se1B	2.316(1)
C1-C2	1.394(17)
C1-C6	1.389(13)
C2-C3	1.363(18)
C3-C4	1.347(16)
C4-C5	1.372(19)
C5-C6	1.393(15)
C6-C7	1.490(16)
C7-N1	1.374(14)
C7-O1	1.197(15)
C8-C9	1.392(14)
C8-C13	1.374(19)
C8-N1	1.432(14)
C9-C10	1.377(19)
C10-C11	1.380(21)
C11-C12	1.366(17)
C12-C13	1.356(21)

TABLE IV Selected bond angles (°)

(a) N,N'-Dimethyl-2,2'-diselenodibenzoamide (DMBS)		
C1-Se1-Se1B	101.7	(1)
C7-N1-C8	123.1	(5)
O1-C7-N1	121.2	(5)
N1-C7-C6	117.8	(4)
O1-C7-C6	121.0	(5)
C7-C6-C1	119.9	(4)
C7-C6-C5	121.4	(5)
Se1-C1-C6	119.8	(4)
Se1-C1-C2	120.8	(4)
(b) N,N'-Diphenyl-2,2'-diselenodibenzoamide (DEBS)		
C1-Se1-Se1B	102.5	(3)
Se1-C1-C6	119.1	(7)
Se1-C1-C2	121.1	(8)
C5-C6-C7	121.8	(9)
C1-C6-C7	119.3	(9)
C6-C7-O1	124	(1)
C6-C7-N1	112.5	(9)
N1-C7-O1	123	(1)
C7-N1-C8	124.1	(8)

TABLE V Selected torsion angles (°)

(a) N,N'-Diphenyl-2,2'-diselenodibenzoamide (DMBS)		
C1 -Se1 -Se1B-C1B	−82.4	(2)
Se1B-Se1 -C1–C6	163.4	(4)
Se1B-Se1 -C1–C2	−16.1	(5)
C8 -N1 -C7–O1	3.1	(8)
C8 -N1 -C7–C6	−178.4	(5)
O1 -C7 -C6–C1	28.9	(7)
(b) N,N'-Diphenyl-2,2'-diselenodibenzoamide (DEBS)		
C1-Se-Se1B-C1B	86.1	(4)
Se1B-Se1-C1–C6	−161.3	(7)
Se1B-Se1-C1–C2	19.1	(9)
C1 -C6 -C7–O1	−37	(1)
C6 -C7 -N1–C8	−178.4	(9)
O1 -C7 -N1–C8	0	(2)

benzene rings which are 72.4(1)° and 90.0(3)° in DMBS and DEBS, respectively. The angle between the planes of the phenyl rings in DEBS is 73.0(3)° whereas the angles between the planes of benzene fragments and phenyl substituents are 84.2(3)°. The dihedral angle between the benzene ring and the plane defined by the four atoms of the amide group is 30.5(3)° in DMBS and 39.8(6)° in DEBS. The same kind of twist of the amide group with respect to the benzene plane was reported for other benzamides[8]. It seems that twist observed in the

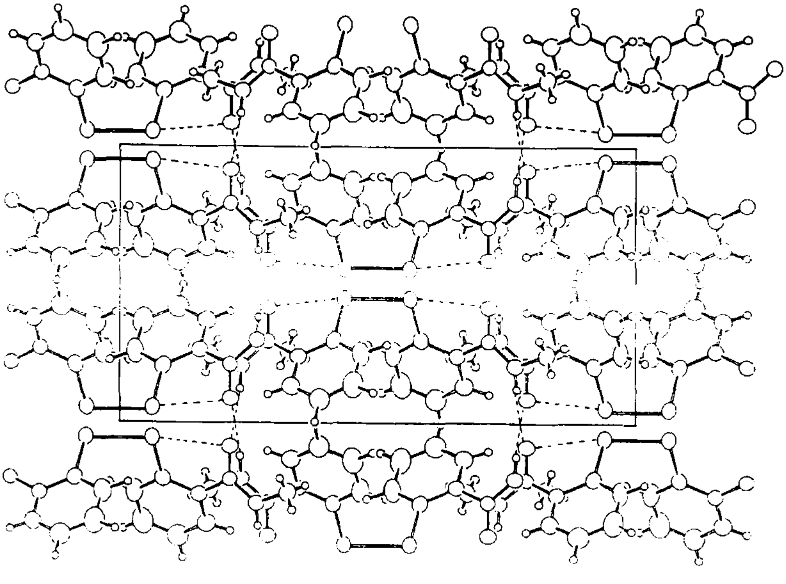


FIGURE 3 The projection of the crystal structure of DMBS on xy plane. Broken lines show the hydrogen bonding and the intermolecular Se···O interactions.

DMBS and DEBS may results both from packing reasons and from the tendency of the carbonyl oxygen atom to form the linear system Se-Se···O. This linear arrangement may be interpreted as a result of hipervalency of selenium[5]. The distances corresponding to Se···O interactions, 2.849(8)Å in DEBS and 2.742(5)Å in DMBS, are longer than the standard covalent Se-O bond but, on the other hand, they are much shorter than the sum of Van der Waals radii which is 3.4Å. The angles of the type of Se-Se···O are 173.71(19)° for DEBS and 173.55(8)° for DMBS. A similar phenomenon was reported by Iwasaki at al.[5] for a sulfur analogue of DMBS, N,N′-dimethyl-2,2′-dithiodibenzoamide (DMBT). In this compound two selenium atoms are replaced with sulfur atoms, the relevant bond lengths and angles are S-S = 2.042(1)Å, S-C_{AR} = 1.792(2)Å, C_{ar}-S-S = 104.74(5)°, S-S..O = 173.52(4)°, Se···O = 2.896(1)Å and C_{ar}-S-S-C_{ar} = 88.04(7). The dihedral angle between the benzene ring and the plane defined by the four atoms of the amide group is 44.3(1)° in DMBT.

Besides Se···O short contacts, O···H intramolecular interactions were also observed with H atoms belonging to the substituents (-CH_3 in DMBS and -C_6H_5 in DEBS). The distances corresponding to these interactions are 2.64(8)Å in DEBS and 2.59(6)Å in DMBS. The angles of type Se···O···H are 173(2)° in DEBS and 136(1)° in DMBS.

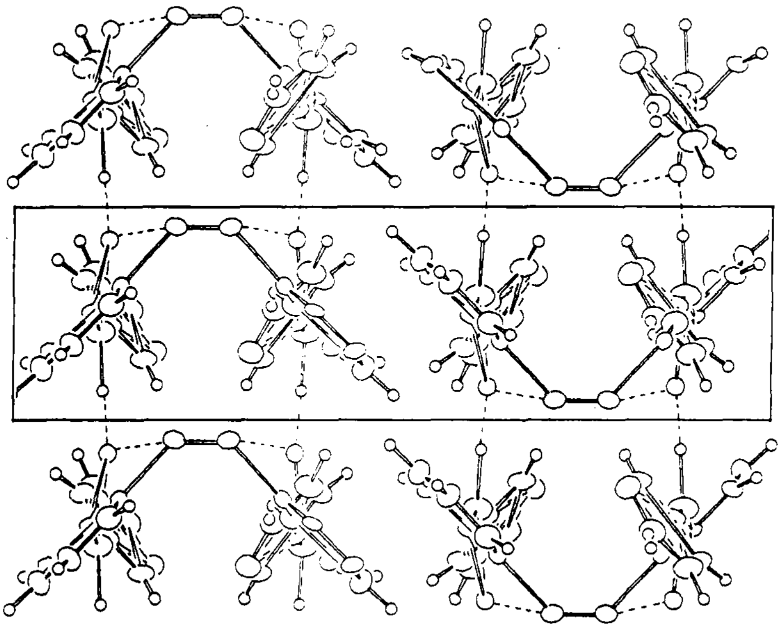


FIGURE 4 The projection of the crystal structure of DEBS on yz plane. The molecules with the symmetry opperation involving x + 0.5 are omitted. Broken lines show the hydrogen bonding and the intermolecular Se···O interactions.

In both diselenide structures the O atom is involved not only in the intramolecular Se···O interactions but also in intermolecular, N-H···O, hydrogen bonds. The parameters of these hydrogen bonds are:

in DMBS:

N1-H1	H1···O1(ii)	N1···O1(ii)	N1-H1···O1(ii)
0.86(06)Å	2.03(6)Å	2.864(6)Å	161 (5)°

ii = (−x + 0.5, y + 0.5, −z + 0.5)

in DEBS:

N1-H5	H5···O1(ii)	N1···O1(ii)	N1-H5···O1(ii)
1.46(13)Å	1.53(13)Å	2.962(12)Å	176 (8)°

ii = (x, y + 1.0, z)

For a comparison parameters of the same kind of hydrogen bonds in DMBT are: O1···N1(ii) = 2.818(2)Å, O1···H1(ii) = 2.03(2)Å, O1···N1(ii)-H1(ii) = 163(2)°[5].

Fig. 3 and 4 depict the arrangement of molecules in the unit cells of DMBS and DEBS crystals, projected on xy plane for DMBS and on yz plane for DEBS. These packings, as well as that in DMBT, are dominated by ribbons parallel to y axis, formed *via* the intermolecular hydrogen bonds, N-H···O. The molecules connected by the hydrogen bonds are interrelated differently in DEBS and DMBS. In the first case the relation between linked molecules is the 5.04Å translation along y axis discussed by Bernstein et al.[6] for *trans*-amides as "a very prevalent in nature". The same relation was found in DMBT where the length of b is 4.92Å. In the second case, i.e. in DMBS, the molecules are related by 2_1 axis, with the translation of 9.606(4)Å, which is also a packing motif often observed in the crystalline structures of N-monosubstituted *trans*-amides R_C-$CONHR_N$[8]. These dissimilarities in the molecular arrangements in the studied structures are accompanied by differences in the mutual orientations of the hydrogen-bonded amide planes and the collinearity of the C═O and O···N directions. In DEBS the amide planes, related by translation, are parallel while in DMBS the angle between these planes, related by 2_1 axis, is 32.74°. In both structures the C═O and O···N bonds tend to be collinear with the angles between them equal 166.44 and 150.48 in DEBS and DMBS, respectively.

The other feature of the molecular packing worth mentioning is the arrangement of Se-Se bonds which are parallel to the a translation in DMBS and c in DMBT whose lengths are very similar, i.e. 18.29Å and 18.73Å, respectively. In DEBS Se-Se bonds are approximately parallel to the direction [101] with the translation of 28.35Å.

The difference between DMBS and DMBT is quite surprising. Both molecules are isosterical and present very close geometrical similarity, but the spacial arrangement of their molecules is different though the volumes of their unit cells are quite comparable i.e. 1651.6(9) and 1593.0(6)Å^3, respectively.

The structure analysis of DEBS, DMBS and its sulfur analogue leads to the conclusion that the conformation of the diselenide and disulfide molecules may be a result of the interplay between two tendencies. One of them consists in linear intramolecular arrangements of chalcogen-chalcogen···O and the other involves formation of intermolecular N-H···O hydrogen bonds with preferably collinear C═O, O···N directions.

Acknowledgments

We are grateful to Dr J. Grochowski (Regional Laboratory of Physicochemical Analysis and Structure Research) for difficult, non-routine diffractometric measurement of a very small DEBS crystal. We also would like to acknowledge the guiding assistance of Dr K. Stadnicka during the whole experiment. Special thanks to Prof. B. Oleksyn and J. Śliwiński for intensive discussions.

This work was supported by grant of Polish State Committee for Science Research (KBN) under project No. PB/1199/P3/93/94.

References

[1] G. R. M. M. Haenen, B. M. De Rooij, N. P. E. Vermeulen and A. Bast, *Mol. Pharmacol.*, **37**, 412–422 (1989).
[2] R. Morgenstern, I. A. Cotgreave and L. Engman, *Chem-Biol. Interactions*, **84**, 77–84 (1992).
[3] O. Epp, R. Ladenstein and A. Wendel, *Eur. J. Biochem.*, **133**, 51–69 (1983).
[4] H.-B. Burgi and J. D. Dunitz "Structure Correlation", edited by H.-B. Burgi and J. D. Dunitz, vol. **2**, (1994).
[5] F. Iwasaki, N. Toyoda and N. Yamazaki, *Acta Cryst.*, **C45**, 1914–1917 (1989).
[6] J. Brenstein, M. C. Etter and L. Leiserowitz, "Structure Correlation", edited by H.-B. Burgi and J. D. Dunitz, vol. **2**, 341–507 (1994).
[7] I. Hargittai and B. Rozsondai, "The Chemistry of Organic Selenium and Tellurium Compounds", edited by S. Patai and Z. Rappaport, vol. **1**, 63–155 (1986).
[8] L. Leiserowitz and M. Tuval, *Acta Cryst.*, **B34**, 1230–1247, (1978).
[9] G. M. Sheldrick, SHELXS-86 Program For Crystal Structure Determination, Cambridge. UK (1986).
[10] G. M. Sheldrick, SHELXL93, Program For the Refinement of Crystal Structures, Univ. of Gottingen, Germany, (1993).
[11] M. Nardelli, PARST95, release May 1995, Comput. Chem., **7**, 95–98 (1983).
[12] C. K. Johnson, ORTEP-II, Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA (1976).

Endnotes

1. List of structure factors, anisotropic temperature factors for non-H atoms and atomic parameters for H atoms have been deposited with the Brithish Library Document Supply Centre as Supplementary Publications No···. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England