A Structural Study of Selenobenzamides: Crystal Structures and Dynamic ^{13}C NMR

Pieter A. Otten, Syb Gorter, and Arne van der Gen*

Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University,
P. O. Box 9502, NL-2300 RA Leiden, The Netherlands

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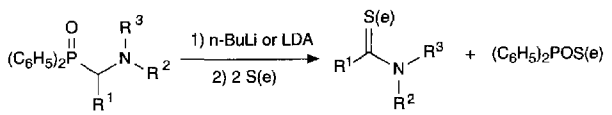
The solid-state structures of (*p*-bromoselenobenzoyl)morpholine (**2a**) and [*p*-(dimethylamino)selenobenzoyl]morpholine (**2b**) were determined by X-ray diffraction. Both molecules show a flat selenoamide group. The larger contribution of resonance stabilization by the aromatic ring carrying the *p*-dimethylamino substituent is reflected by the smaller interplanar angle Θ between the aromatic ring and the selenoamide group [53.3(1)° vs. 81.1(1)°] and by the shorter length of the C=Se bond [1.824(5) Å vs. 1.840(3) Å]. The Gibbs free energy of activation of C–N bond rotation ($\Delta G^{\ddagger}_{rot}$) of five *p*-substituted (selenobenzoyl)morpholines was determined by dynamic ^{13}C NMR. The activation barriers were found to range from 61.6 kJ/mol (X = $NNMe_2$) to 75.1 kJ/mol (X = H). The $\Delta G^{\ddagger}_{rot}$ values of the corresponding (thiobenzoyl)morpholines were found to be from 3.2 kJ/mol (X = NMe_2) to 5.0 kJ/mol (X = H) lower. In both cases, $\Delta G^{\ddagger}_{rot}$ showed an excellent linear Hammett correlation with σ_p^+.

Introduction

We previously reported the synthesis of tertiary thioamides **1** and tertiary selenoamides **2** by reaction of the lithiated anions of α-amino-substituted diphenylphosphine oxides **3** with two equivalents of elemental sulfur or selenium[1] (Scheme 1). A mechanism was presented to account for the observed stoichiometry of the reaction[1]. So far, the reaction of **3**-Li with elemental selenium is the most generally applicable route to tertiary selenoamides **2**, as virtually all structural types of these selenocarbonyl compounds of excellent purity could be prepared in good yields[1]. This opened the possibility of investigating the 3-dimensional structure of these compounds by X-ray diffraction and of studying the rotational barrier of the C–N bond by dynamic ^{13}C NMR.

Scheme 1



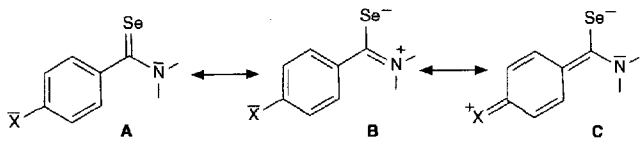
3 **1, 2**

R^1=H, alkyl, aryl and alkenyl

R^2,R^3=$(CH_2)_2O(CH_2)_2$; $(CH_2)_4$; Ph, Me; Me, Me

Two of the easily crystallizable selenobenzamides, 4-(*p*-bromoselenobenzoyl)morpholine (**2a**) and 4-[*p*-(dimethylamino)selenobenzoyl]morpholine (**2b**) were subjected to an X-ray structure determination. The C–N bond of a selenoamide possesses partial double-bond character because the (normally highly reactive[2]) selenocarbonyl bond is stabilized by conjugation with the free electron pair at nitrogen (canonical structure B, Figure 1). A priori, the X-ray structures of **2a** and **2b** were therefore expected to reveal a planar selenoamide group (Se, C, N and the two methylene substituents at nitrogen in one plane). The structural parameters of **2a** and **2b** will be discussed and compared with crystallographic data of structurally related compounds.

Figure 1. Canonical structures of *p*-substituted selenobenzamides



The double bond character of the C–N bond in selenoamides results in hindered rotation around this bond. If rotation is slow on the NMR time scale, then the magnetic inequivalence of further substituents at nitrogen, such as the α-methylene groups in the (selenobenzoyl)morpholines studied here, can be visualized by NMR. Rotation around the C–N bond of a selenoamide requires loss of conjugation between the selenocarbonyl group and the free electron pair at nitrogen. In the transition state of the rotational process, resonance stabilization of the free selenocarbonyl group can be provided by an adjacent (*p*-substituted) aromatic ring, as depicted in canonical structure C (Figure 1). As a consequence, a more strongly electron-donating substituent X on the aromatic ring will lower the free energy of activation for C–N bond rotation and thereby the temperature at which coalescence of the NMR signals will be observed, assuming that Δν (see below) is approximately constant for compounds with different substituents X. The free energy of activation of bond rotation, $\Delta G^{\ddagger}_{rot}$, at coalescence temperature (T_c) can be calculated using the Eyring equation[3].

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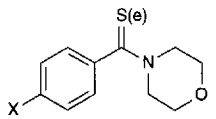
$$\Delta G^{\ddagger}_{rot} = 19.5 \cdot T_c \cdot [9.971 + \log(T_c/\Delta\nu)]$$

where $\Delta\nu$ is defined as the chemical shift difference (in Hz) at T_c between the NMR signals under investigation. The $\Delta G^{\ddagger}_{rot}$ values of five *p*-substituted (selenobenzoyl)morpholines [*p*-$XC_6H_4C(=Se)NCH_2CH_2OCH_2CH_2$; with X = NMe_2, OMe, SMe, Me, and H (**2b–f**)] were determined[4]. $CDCl_3$ was used as the solvent. Coalescence of the well-separated ^{13}C-NMR signals of the *syn*- and *anti*-methylene carbon atoms[5] at nitrogen in selenobenzamides **2b–f** allowed accurate determination of T_c[6]. For reasons of comparison, the $\Delta G^{\ddagger}_{rot}$ values of the corresponding (thiobenzoyl)morpholines were also determined.

Results and Discussion

Structures of Compounds 2a and 2b in the Solid State

Crystals of selenobenzamides **2a** and **2b**, suitable for X-ray structure determination, were obtained by careful crystallization from toluene. The crystal data of both compounds are presented in Table 1.



2a: X=Br

2b: X=Me_2N

Table 1. Crystal data of **2a** and **2b**: e.s.d.'s are given in parentheses

	2a	**2b**
Formula	$C_{11}H_{12}BrNOSe$	$C_{13}H_{18}N_2OSe$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/a$
a	7.139(2) Å	10.698(1) Å
b	14.238(4) Å	12.0240(6) Å
c	11.796(4) Å	11.5237(5) Å
β	95.78(3)°	114.102(5)°
Z	4	4
ρ (calcd.)	1.855 kg/dm^3	1.459 kg/dm^3
F(000)	647.9	607.9
V (unit cell)	1192.9(6) Å^3	1353.1(1) Å^3
Color	pale yellow	orange-yellow

A perspective view (ORTEP plot) of compound **2a**, together with the adopted numbering scheme, is shown in Figure 2. Selected bond lengths, bond angles and dihedral angles of **2a** are presented in Table 2.

As expected, the atoms which constitute the selenoamide bond in **2a**, Se C(5) and N, together with C(1) and C(4), build up a nearly planar arrangement. The dihedral angles between the C(5)–Se bond and the N–C(1) and N–C(4) bonds of 4.3(6)° and 175.7(3)°, respectively, underline this fact. Additional support for the planarity of the selenoamide moiety comes from the small displacements of the Se, N, C(5), C(1) and C(4) atoms from the best-fitting plane through these five atoms (Table 3). The sum of the bond angles around the nitrogen atom (359.5°) confirms its sp^2-hybridization. Furthermore, the relatively short C(5)–N

Figure 2. ORTEP view of selenobenzamide **2a** (30% probability ellipsoids)

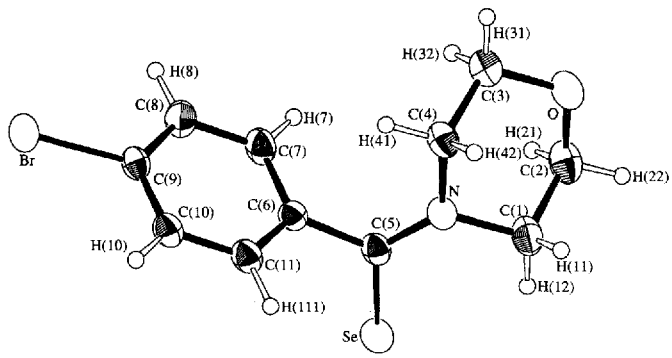


Table 2. Selected geometric data of **2a**: e.s.d.'s are given in parentheses

Bond lengths (Å)			
C(5)–Se	1.824(5)	N–C(4)	1.476(6)
C(5)–N	1.324(5)	N–C(1)	1.473(6)
C(5)–C(6)	1.500(6)	C(9)–Br	1.912(4)
Bond angles (°)			
N–C(5)–C(6)	117.7(4)	C(5)–N–C(4)	126.3(4)
N–C(5)–Se	125.3(3)	C(5)–N–C(1)	123.0(4)
Se–C(5)–C(6)	117.0(3)	C(1)–N–C(4)	110.2(3)
Dihedral angles (°)			
Se–C(5)–N–C(1)	4.3(6)	Se–C(5)–C(6)–C(7)	–96.9(4)
Se–C(5)–N–C(4)	–175.7(3)	Se–C(5)–C(6)–C(11)	81.0(4)

bond length of 1.324(5) Å indicates partial double bond character [cf. average $C(sp^3)–N(sp^3)$ 1.469 Å, average $C(sp^2)–N(sp^2)$ = 1.279 Å (aromatic imines)[7]. The sp^2-hybridization at C(5) is likewise clear from the sum of its bond angles (360.0°). The C(5)–Se bond length in selenoamide **2a** of 1.824(5) Å is close to C=Se bond lengths previously observed for other selenoamides (vide infra).

Table 3. Displacements (*d*) from the plane of the selenoamide group in **2a** and **2b**: e.s.d's are given in parentheses

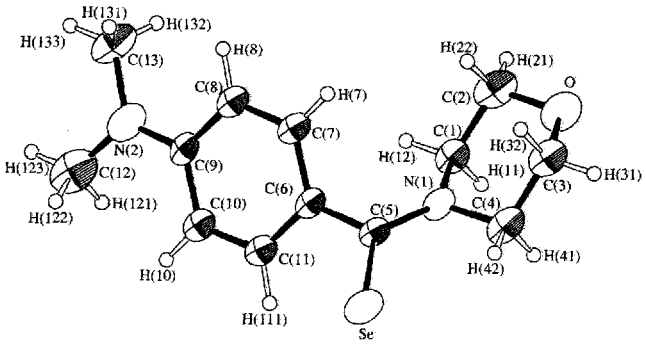
Atom	*d* (Å) **2a**	*d* (Å) **2b**
Se	0.001(1)	–0.008(1)
C(5)	–0.006(5)	0.111(4)
N	–0.041(4)	0.063(4)
C(1)	0.014(7)	–0.156(5)
C(4)	0.041(6)	0.033(6)

The morpholino ring in **2a** adopts a chair-like conformation. The C(1)–N–C(4) bond angle is contracted to 110.2(3)°, thereby fulfilling the angular requirements for a chair-like conformation of the morpholino ring. At the same time, the accompanying increased bond angles C(5)–N–C(1) [of 123.0(4)°] and C(5)–N–C(4) of [126.3(4)°] somewhat decrease the steric interaction between C(1) and Se and between C(4) and the aromatic ring, respectively. A noteworthy structural feature of selenobenza-

mide **2a** is the almost right angle, $\Theta = 81.1(1)°$, between the plane of the selenoamide group and the *p*-bromo-substituted aromatic ring. Conjugation between these two π-systems, i.e. the contribution of canonical structure C to the bonding in **2a**, appears to be virtually absent in the solid state. This large value of the interplanar angle Θ probably arises from steric congestion between the aromatic ring and the sizeable selenoamide moiety. The interplanar angles of structurally related *p*-bromo-*N*,*N*-dimethylbenzamide[8a] and *N*,*N*-dimethylthiobenzamide[8b] were determined by X-ray analysis to be 46° and 63°, respectively. Evidently, a further increase in the van der Waals' radius of the chalcogen atom induces a corresponding increase in the interplanar angle Θ.

An ORTEP plot of selenobenzamide **2b**, depicted in Figure 3, shows a perspective view of the molecule, along with the adopted numbering scheme.

Figure 3. ORTEP view of selenobenzamide **2b** (30% probability ellipsoids)



The structural features of the selenomorpholido moiety in selenobenzamide **2b** are virtually identical to those observed for **2a**. The selenoamide group, defined by Se, C(5) and N(1), together with C(1) and C(4) again constitute an almost-planar atomic array, although the deviations from planarity are somewhat larger than those found in **2a**. Table 3 lists the displacements of these five atoms from the best-fitting plane. The C=Se bond of **2b** [1.840(3) Å] is slightly longer than the C=Se bond in selenobenzamide **2a** [1.824(5) Å]. As before, the morpholino ring adopts a chair-like conformation.

A difference between the structures of the two selenoamides can be found in the positioning of the phenyl rings. The angle Θ between the plane of the selenoamide group and the *p*-amino-substituted aromatic ring in **2b** is 53.3(1)°, which is substantially smaller than the angle observed for its *p*-bromo-substituted analog **2a** [81.1(1)°]. This decreased interplanar angle allows some resonance stabilization of the selenoamide group in **2b** by the electron-donating aromatic ring. The longer C=Se bond and the shorter C_{ipso}–C(=Se) bond in **2b** compared to **2a** (see Tables 2 and 4) are consistent with some participation of resonance structure C (Figure 1) in the bonding in **2b** in the solid state.

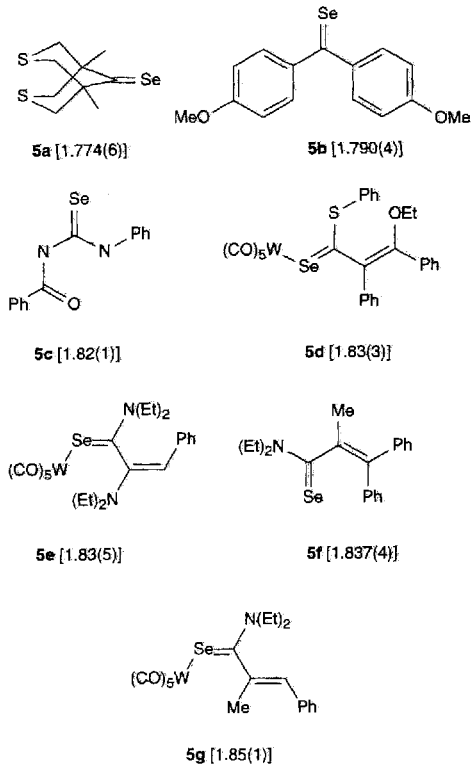
The structures and C=Se bond lengths of the selenocarbonyl compounds for which the crystal structures have previously been reported are compiled in Figure 4. The

Table 4. Selected geometric data of **2b**: e.s.d.'s are given in parentheses

Bond lengths (Å)			
C(5)–Se	1.840(3)	N(1)–C(1)	1.467(4)
C(5)–N(1)	1.331(5)	N(1)–C(4)	1.464(5)
C(5)–C(6)	1.476(5)	C(9)–N(2)	1.365(5)
Bond angles (°)			
N(1)–C(5)–C(6)	118.9(3)	C(5)–N(1)–C(1)	125.6(3)
N(1)–C(5)–Se	123.0(2)	C(5)–N(1)–C(4)	123.4(3)
Se–C(5)–C(6)	118.1(3)	C(1)–N(1)–C(4)	110.5(3)
Dihedral angles (°)			
Se–C(5)–N(1)–C(1)	−165.1(3)	Se–C(5)–C(6)–C(11)	50.3(3)
Se–C(5)–N(1)–C(4)	5.7(5)	C(12)–N(2)–C(9)–C(10)	−5.8(5)
Se–C(5)–C(6)–C(7)	−127.6(3)	C(13)–N(2)–C(9)–C(8)	−2.2(5)

shortest selenocarbonyl bond known [1.774(6) Å], was found in sterically encumbered selenoketone **5a**[9a]. Elongation of the C=Se bond in stable, monomeric, selenoketone **5b** resulted from resonance with the *p*-methoxyphenyl rings[9b]. For compounds **5c**–**g**[9c–g], which contain a selenocarbonyl group that is stabilized by conjugation with the free electron pairs at the nitrogen (selenoamides **5c** and **5e**–**g**)[9c,9e–g] or sulfur atom (metalcoordinated selenothio(*S*) ester **5d**)[9d], a further increase in the C=Se bond length was observed. The decreased bond order of the C=Se bond underlines the contribution of resonance structure B (Figure 1) to the bonding in selenoamides.

Figure 4. Selenocarbonyl compounds **5a**–**g**: C=Se bond lengths (Å) are given in parentheses



The C=Se bond lengths found for selenobenzamides **2a** [1.824(5) Å] and **2b** [1.840(3) Å], are consistent with the reported C=Se bond lengths in selenoamides **5c**, **5e–g**. Likewise, the C–N bond lengths observed for **2a** [1.324(5) Å] and **2b** [1.331(5) Å] are comparable to those found in **5c** [1.32(1) Å][9c], **5e** [1.301(8) Å][9l], **5f** [1.329(7) Å][9g] and **5g** [1.33(2) Å][9g]. In the solid-state structures of selenoamides **5e–g**, large interplanar angles between the selenoamide group and the adjacent double bond were found [82.0(7)° (**5e**), 66.5° (**5f**) and 89.0° (**5g**)][9d–f], excluding substantial conjugation[10].

Hindered Rotation in (Thiobenzoyl)morpholines 1b–f and (Selenobenzoyl)morpholines 2b–f

The coalescence temperatures (T_c) of (thiobenzoyl)morpholines **1b–f** and (selenobenzoyl)morpholines **2b–f** were determined using $CDCl_3$ as solvent. The values of T_c could be accurately determined within 1 K and proved to be reproducible. They are listed in Tables 5 and 6, together with the observed values of $\Delta\nu$ between the ^{13}C signals of the *syn*- and *anti*-NCH_2 groups and the calculated values of $\Delta G^{\ddagger}_{rot}$. The values of $\Delta\nu$, used in the Eyring equation, were determined at a temperature 40–60 K below T_c and proved to be constant over a large temperature range, thus allowing their use in the equation. The $\Delta G^{\ddagger}_{rot}$ values of (thiobenzoyl)-morpholines **1b–f** and (selenobenzoyl)morpholines **2b–f** were subjected to a correlation analysis[3,11] using a modified set of Hammett constants σ_p^+. This set of Hammett constants has been defined by Brown and Okamoto for situations where a center with strong acceptor character develops next to a *p*-substituted aromatic ring[12]. The highly polarizable π-bond of the selenocarbonyl group (as a result of weak overlap of the carbon 2*p* orbital and the selenium 4*p* orbital)[13] might well fit this description.

Table 5. $\Delta G^{\ddagger}_{rot}$ values of (thiobenzoyl)morpholines **1b–f**

X	σ^+_p		Δν (Hz)	T_c (K)	$\Delta G^{\ddagger}_{rot.}$ (kJ/mol)
NMe_2	–1.7	**1b**	140.71	296	58.4
OMe	–0.78	**1c**	139.20	328	64.5
SMe	–0.6	**1d**	146.53	336	66.5
Me	–0.3	**1e**	145.07	341	67.5
H	0	**1f**	149.47	354	70.1

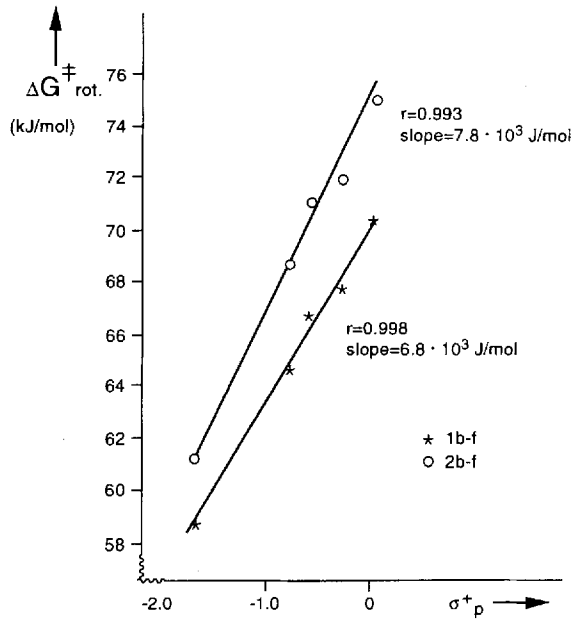
Table 6. $\Delta G^{\ddagger}_{rot}$ values of (selenobenzoyl)morpholines **2b–f**

X	σ^+_p		Δν (Hz)	T_c (K)	$\Delta G^{\ddagger}_{rot.}$ (kJ/mol)
NMe_2	–1.7	**2b**	38.10	296	61.6
OMe	–0.78	**2c**	35.17	328	68.7
SMe	–0.6	**2d**	24.91	334	71.0
Me	–0.3	**2e**	27.85	340	72.0
H	0	**2f**	21.98	351	75.1

The results in Tables 5 and 6 clearly show that the free energy of activation of C–N bond rotation of *p*-substituted selenobenzamides **2b–f** is higher (by 3.2–5.0 kJ/mol) than that of their thio analogs **1b–f**. This can be ascribed to a larger contribution of canonical structure B (Figure 1) to the bonding in selenoamides than in thioamides, because rotation around the C–N bond is accompanied by loss of conjugation. An increase of $\Delta G^{\ddagger}_{rot}$ was also noted upon going from an amide to its corresponding thioamide[14]. This trend held for a large range of amides and the accompanying increase of $\Delta G^{\ddagger}_{rot}$ was found to be between 8.4 and 16.7 kJ/mol. These values suggest that the gain of stabilization of the carbon-chalcogen bond (by conjugation with the free electron pair at nitrogen) upon going from an amide to its corresponding thioamide is more pronounced than the subsequent step from thioamide to selenoamide.

In Figure 5, Hammett plots are presented for the free energy of activation of C–N bond rotation in (thiobenzoyl)morpholines **1b–f** and (selenobenzoyl)morpholines **2b–f**. In both cases, an excellent linear relationship between σ_p^+ and $\Delta G^{\ddagger}_{rot}$ was found, with correlation coefficients (*r*) of 0.998 and 0.993, respectively. Thus, as anticipated, the free thio- and selenocarbonyl groups, which result upon C–N bond rotation from loss of conjugation with the free electron pair at nitrogen, exert a strong electron demand on the adjacent *p*-substituted aromatic ring. The outcome of this dynamic NMR study clearly demonstates that canonical structure C (Figure 1) effectively participates in describing the bonding in selenobenzamides (and thiobenzamides) in solution. Furthermore it should be noted that for selenobenzamides **2b–f** the sensitivity of $\Delta G^{\ddagger}_{rot}$ to σ_p^+, visualized by the slope of the Hammett plot in Figure 5, is higher than that observed for thiobenzamides **1b–f**. Evidently, the selenobenzoyl system is better capable of transferring electronic effects, induced by the *p*-substituent X, to the chalcogen. This can be readily explained by the higher polarizability of the selenocarbonyl bond in selenobenzamides **2b–f**, as compared to the thiocarbonyl bond[13].

Figure 5. Hammett plots of **1b–f** and **2b–f**



Experimental Section

Synthesis of Thio- and Selenobenzamides: Thiobenzamides **1b–f** and selenobenzamides **2a–f** were prepared according to literature procedures[1].

X-ray Analyses: Reflections were obtained on an Enraf-Nonius CAD-4 four-circle diffractometer, using graphite-monochromatized radiation. Corrections were made for Lorentz and polarization effects. Empirical corrections were made for absorption effects. The structures of **2a** and **2b** were solved using XTAL 3.2 and programs written or modified by *S. Gorter, R. A. G. de Graaff* and *E. W. Rutten-Keulemans*, Leiden Institute of Chemistry. In the case of **2a**, the heavy atoms (Se, Br) were located by direct methods, then the other non-H atoms were located by Fourier methods. All non-H atoms of **2b** were located by direct methods. For refinement of both structures, the H atoms were placed at 1.00 Å from their parent atoms, followed by a least-squares refinement (anisotropic), on *F*, of the positional parameters of the non-H atoms with the H atoms coupled. Scattering factors and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography* (**1974**, vol. IV). More details on the data collection and structure refinement are presented in Table 7. The non-hydrogen fractional coordinates and isotropic parameters of **2a** and **2b** are collected in Tables 8 and 9.

Table 7. Details of the data collection and structure refinement for compounds **2a** and **2b**

	2a	**2b**
T (K)	297	293
Solvent	Toluene	Toluene
Crystal size (mm^3)	0.65 × 0.30 × 0.20	0.6 × 0.2 × 0.15
Radiation, λ (Å)	Mo($K\alpha$), 0.71073	Cu($K\alpha$), 1.54178
θ_{min}, θ_{max} (°)	2.0, 30	2.5, 75
Scan type	ω/θ	$\omega/2\theta$
Data set	h ±10, k 0:20, l 0:16	h −13:0, k 0:15, l ±14
Total data	4012	2928
Observed data, [$I > 2\sigma(I)$]	1761	2395
Reflections for refinement	1760	2385
No of refined parameters	138	156
Weighting scheme	$1/\sigma^2(F)$	$1/\sigma^2(F)$
Final R, wR	0.036, 0.036	0.046, 0.055
$(\Delta/\sigma)_{av}$	0.0008387	0.0004048
$Dens_{min, max}$ in final diff. Fourier ($eÅ^{-3}$)	−1.15, 0.77	−0.92, 0.95

Table 8. Non-hydrogen fractional coordinates and anisotropic displacement parameters (U_{eq}) of **2a**

	x/a	y/b	z/c	U_{eq} (Å^2)[a]
Br	1.40328(7)	0.44181(3)	0.63553(5)	0.0573(2)
Se	0.74584(7)	0.75608(3)	0.83809(4)	0.0520(2)
O	0.7502(5)	0.9654(2)	0.4774(3)	0.056(1)
N	0.7338(5)	0.7981(2)	0.6052(3)	0.044(1)
C(1)	0.6008(7)	0.8756(3)	0.6179(4)	0.057(2)
C(2)	0.6967(8)	0.9659(3)	0.5910(4)	0.061(2)
C(3)	0.8763(7)	0.8898(3)	0.4632(4)	0.054(2)
C(4)	0.7893(7)	0.7961(3)	0.4881(4)	0.047(2)
C(5)	0.8066(6)	0.7465(3)	0.6920(4)	0.041(1)
C(6)	0.9519(6)	0.6747(3)	0.6693(3)	0.038(1)
C(7)	1.1374(7)	0.6993(3)	0.6664(4)	0.050(2)
C(8)	1.2747(6)	0.6314(3)	0.6532(4)	0.052(2)
C(9)	1.2176(6)	0.5380(3)	0.6415(3)	0.038(1)
C(10)	1.0328(6)	0.5130(3)	0.6411(4)	0.044(2)
C(11)	0.9009(6)	0.5815(3)	0.6544(4)	0.044(2)

[a] $U_{eq} = 1/3\ \Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

Complete data of the X-ray structure analyses were deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. This material can be ordered on quoting the deposition number 100002.

Dynamic ^{13}C NMR: ^{13}C-NMR spectra (50 MHz) were recorded on a Jeol NM FX-200 spectrometer, equipped with a NM-PVTS (Jeol) temperature controller. Calibration was performed using an ethylene glycol sensor[15]. The coalescence temperatures could be determined within one degree by analysis of the ^{13}C-NMR signals of the NCH_2 groups. In all cases studied, the coalescence temperatures proved to be reproducible. 0.1 M solutions of thiobenzamides **1b–f** and selenobenzamides **2b–f** in $CDCl_3$ were used and the deuterated solvent was used for internal lock and as an internal standard.

Table 9. Non-hydrogen fractional coordinates and anisotropic displacement parameters (U_{eq}) of **2b**

	x/a	y/b	z/c	U_{eq} (Å^2)[a]
Se	0.33583(5)	0.08999(3)	0.22254(4)	0.0581(2)
N(1)	0.3525(3)	0.2327(2)	0.0377(2)	0.046(1)
N(2)	0.3259(4)	0.6205(3)	0.4105(3)	0.060(1)
O	0.4512(3)	0.2578(2)	−0.1556(3)	0.067(1)
C(1)	0.3288(4)	0.3345(3)	−0.0386(3)	0.051(1)
C(2)	0.4417(5)	0.3515(3)	−0.0827(4)	0.064(2)
C(3)	0.4741(4)	0.1586(3)	−0.0825(4)	0.061(2)
C(4)	0.3661(4)	0.1368(3)	−0.0344(3)	0.058(2)
C(5)	0.3452(3)	0.2243(3)	0.1500(3)	0.041(1)
C(6)	0.3424(4)	0.3269(3)	0.2191(3)	0.042(1)
C(7)	0.4416(4)	0.4099(3)	0.2453(3)	0.045(1)
C(8)	0.4395(4)	0.5048(3)	0.3104(3)	0.045(1)
C(9)	0.3342(4)	0.5238(3)	0.3521(3)	0.045(1)
C(10)	0.2357(4)	0.4387(3)	0.3285(3)	0.048(1)
C(11)	0.2414(4)	0.3434(3)	0.2651(3)	0.045(1)
C(12)	0.2248(5)	0.6363(4)	0.4608(4)	0.082(2)
C(13)	0.4218(5)	0.7100(3)	0.4285(4)	0.074(2)

[a] $U_{eq} = 1/3\ \Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

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[4] So far only the values of ΔG^{+}_{rot} of a series of selenoureas $H_2NC(=Se)NR_2$ have been reported. The activation barriers, which ranged from 40.6 kJ/mol to 67.2 kJ/mol, strongly depended on the nature of the amino substituent. The lowest values for ΔG^{+}_{rot} were found for piperidino (R–R = $-[CH_2]_5-$) and morpholino (R–R = $-[CH_2]_2O[CH_2]_2-$) substituents, see: S. Behrendt, R. Borsdorf, E. Kleinpeter, D. Gruendel, A. Hantschmann, *Z. Chem.* **1976**, *16*, 405.

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[11] One may object to the use of ΔG^{+}_{rot}, determined at different temperatures for different substituents X, in a Hammett treatment, because this parameter contains a temperature-dependent entropy term: $-T_c\Delta S^{+}_{rot}$. It is known, however, that ΔS^{+}_{rot} for C–N bond rotation in thioamides is relatively low: of the order of 0.8–40 J/molK. The ΔS^{+}_{rot} of structurally related selenoamides is expected to be of the same order of magnitude. Considering the range of T_c values (55 K) found for selenobenzamides **2b–f**, a possible linear correlation between ΔG^{+}_{rot} and σ^{+}_{p} will hardly be affected by T_c. For values of ΔS^{+}_{rot} of thioamides see: [11a] J. Sandström, *J. Phys. Chem.* **1967**, *71*, 2318. – [11b] W. Walter, E. Schaumann, *Chem. Ber.* **1971**, *104*, 3361. – [11c] R. F. Hobson, L. W. Reeves, K. N. Shaw, *J. Phys. Chem.* **1973**, *77*, 1228. – [11d] R. C. Neumann, Jr., V. Jonas, *J. Org. Chem.* **1974**, *39*, 929.

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