24. An Unexpected Isomerization of *N*-Aryl-3-amino-4-nitroisothiazol-5(2*H*)-imines to 2-(Benzothiazol-2-yl)-2-nitroethene-1,1-diamines[1])

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The syntheses of several *N*-aryl-3-amino-4-nitroisothiazol-5(2*H*)-imines **12** from 3,3-diamino-2-nitrothioacrylamides **11** are reported (*Scheme 3*). In polar solvents, a spontaneous isomerization of some of the prepared isothiazol-5(2*H*)-imines **12** yielded benzothiazoles **13** (*Scheme 4*). In the case of 2-alkyl-substituted derivatives of type **12**, the isomerization occurred only at higher temperatures. Electronic influences of different substituents on the rate of the isomerization were studied, and a polar reaction mechanism is proposed in *Scheme 6*. The structures of **12e** and **13e** were established by X-ray crystallography. Conformational analyses of 3-(methylamino)-2-nitro-*N*-phenyl-3-(pyrrolidin-1-yl)thioacrylamide (**11l**) by NMR and X-ray methods were performed with the aim of explaining the distinct behavior of this amide towards Br_2 or diethyl azodicarboxylate.

1. Introduction. – The 3-aminothioacrylamides **1**, synthesized for the first time by *Hennicke* from enamines and isothiocyanates [1], have become useful intermediates in organic syntheses [2–7]. These compounds have found applications as versatile starting materials in heterocyclic chemistry [8] [9], *e.g.*, for the synthesis of thiophenes [10–13], pyrimidines [2] [3] [14], pyrazoles [13], and isothiazoles [3]. Particularly interesting are the 3,3-diamino-2-nitrothioacrylamides **2** [8] [15], prepared from the corresponding nitroketene aminals and isothiocyanates, which were used for the synthesis of nitroheterocycles by direct ring-closure reactions [16–21]. In our previous work, we have shown that nitrothioacylamides **3** are useful starting materials for the synthesis of 5-nitropyrimidines of type **4** [22] [23] and 4-nitroisothiazol-5(2*H*)-imines of type **5** [24–26] (*Scheme 1*).

As the desulfurization of the 3,3-diamino-2-nitrothioacrylamides **3** was expected to yield different nitro-substituted compounds such as iminoazetines, ketene imines, and iminopyrimidines (*cf.* [27]), we investigated the course of this reaction. However, instead of the expected products, nitriles of type **7** and *N*-acylamides of type **8** were obtained on treatment of the *S*-methyl derivatives **6** with $Hg(OAc)_2$ in DMF [27] (*Scheme 2*).

Taking into account the known desulfurization of isothiazoles with Ph_3P to give ketene imines [4], we chose 4-nitroisothiazol-5(2*H*)-imines **5** for the same purpose. These isothiazole derivatives have been obtained directly from **2** (R^2 = H) or **3** by oxidative cyclization using Br_2 as the reagent [19] [20] (*cf.* also [28]). During the characterization

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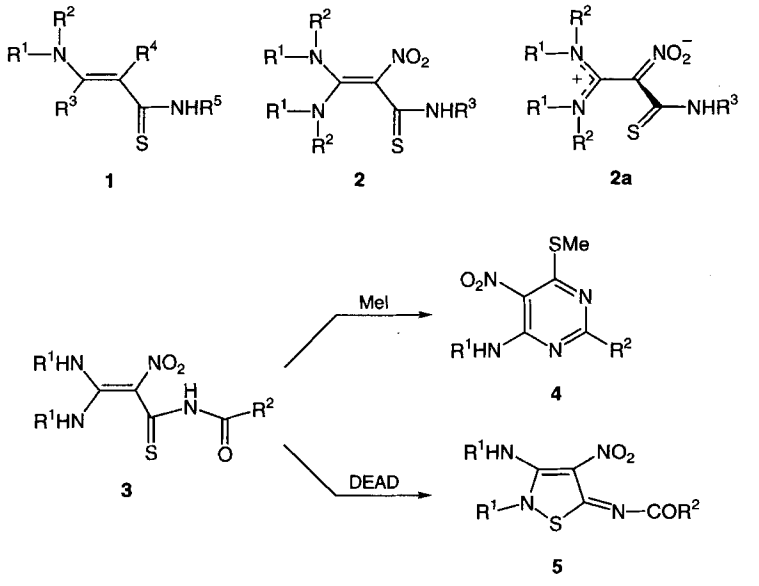
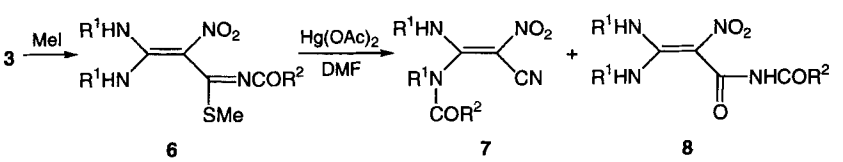
[2]) Part of the planned Ph. D. thesis of *D.M.A.*, Universität Zürich.

Scheme 1[a])



[a]) X-Ray crystallography of 3,3-diamino-2-nitrothioacrylamides of type **2** and **3** showed that there is no C=C bond in their structures; a more likely presentation of **2** is the zwitterion **2a**.

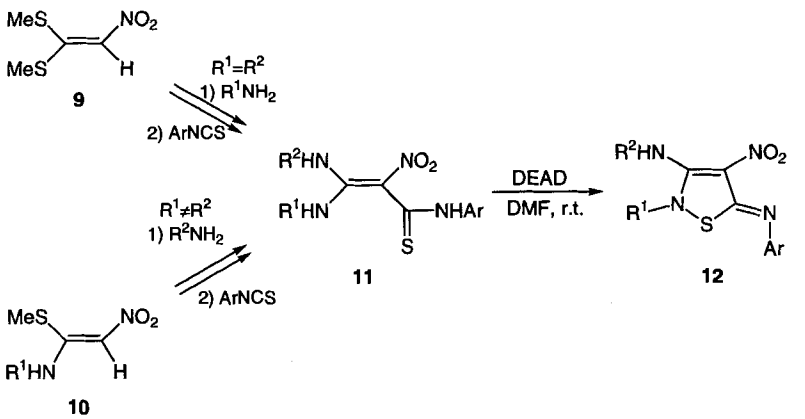
Scheme 2



of the synthesized thiazol-5(2*H*)-imines by NMR spectroscopy, an unexpected isomerization to 2-(benzothiazol-2-yl)-2-nitroethene-1,1-diamines was observed [26]. In this paper, we report on the scope of this reaction. Based on the electronic influence of different substituents, a reaction mechanism is proposed.

2. Results. – 2.1. *Synthesis of* N-*Aryl-3-amino-4-nitroisothiazol-5(2*H*)-imines* **12**. Differently substituted 3,3-diamino-*N*-aryl-2-nitrothioacrylamides **11**, prepared from nitroketene dithioacetal **9** (in the case of $R^1 = R^2$) [29] or from **10** (in the case of $R^1 \neq R^2$) [29] [30] (*cf.* [15]) by consecutive treatment with a primary amine and an aryl isothiocyanate, were treated with diethyl azodicarboxylate (DEAD) in DMF at room temperature. The isothiazol-5(2*H*)-imines **12** were formed *via* an oxidative intramolecular cyclization (*Scheme 3*, *Table 1*) [31]. The use of DEAD as a dehydrogenation reagent [32] [33], instead of Br_2 as previously reported [19] [20], proved to be superior, affording

Scheme 3[a])



[a]) For R^1, R^2, and Ar, see *Table 1*.

Table 1. *Synthesized 3-Amino-*N*-aryl-4-nitroisothiazol-5(2*H*)-imines* **12** *and 2-(Benzothiazol-2-yl)-2-nitroethene-1,1-diamines* **13**

	R^1	R^2	Ar	Yield [%] (from **11**)		R^3	Yield [%] (from **12**)
12a	Ph	Ph	Ph	97	**13a**	H	83
b	4-$MeOC_6H_4$	4-$MeOC_6H_4$	Ph	91	**b**	H	96
c	4-FC_6H_4	4-FC_6H_4	Ph	95	**c**	H	87
d	Ph	Ph	4-$MeOC_6H_4$	75	**d**	MeO	95
e	Ph	Ph	4-$NO_2C_6H_4$	84	**e**	NO_2	61
f	Ph	Me	Ph	44[a])	**f**	H	81
g	Ph	Me	4-$MeOC_6H_4$	48[a])	**g**	MeO	92
h	Me	Ph	Ph	46[a])	**h**	H	82
i	Me	Ph	4-$MeOC_6H_4$	48[a])	**i**	MeO	90
j	$PhCH_2$	$PhCH_2$	Ph	84	**j**	H	81
k	Me	Me	Ph	93	**k**	H	56

[a]) Compounds **12f** and **12h** were formed simultaneously from **11f**, and **12g** and **12i** from **11g**. The compounds were isolated together and separated by column chromatography (*cf. Exper. Part*).

higher yields, shorter reaction times, and easier isolation of the products. Spectroscopic characterization of compounds **12** showed no differences to those synthesized by *Rajappa et al.* using Br_2. The structure of **12e** was established by X-ray crystallography (*Fig. 1* and *Table 2*).

The amino group of **12e** forms an intramolecular H-bond with one of the O-atoms of the NO_2 group at C(4) (N···O 2.615(3) Å, N–H···O 137(2)°) thus forming a six-membered ring. The five-membered isothiazole ring is completely planar; the mean deviation from the plane is 0.0003 Å. The adjacent atoms C(6), N(12), N(18), and N(19) as well as O(3), O(4), C(13), and C(20)[3]) also deviate only slightly (maximum deviation 0.13 Å) from this plane, *i.e.*, the NO_2 group at C(4) is coplanar with the isothiazole ring.

[3]) The arbitrary numbering of the atoms in the ORTEP diagram (*Fig. 1*) is used.

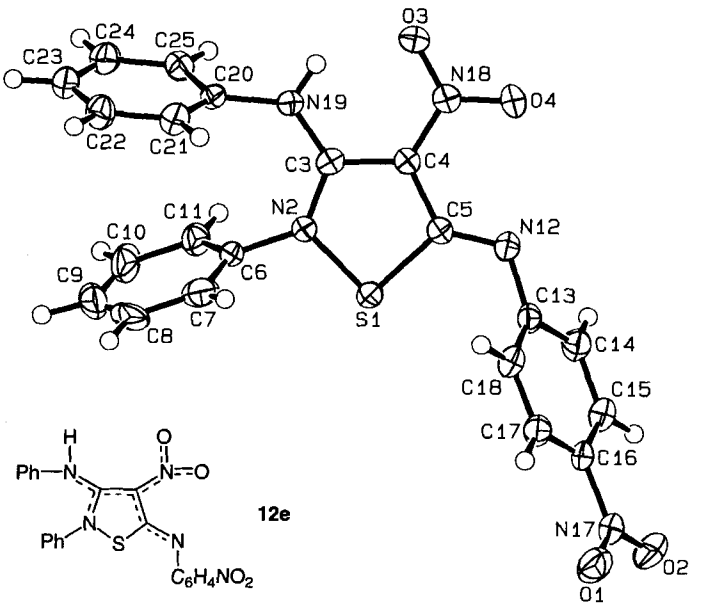


Fig. 1. *ORTEP Plot* [34] *of the molecular structure of* **12e** (arbitrary numbering of the atoms, with 50% probability ellipsoids)

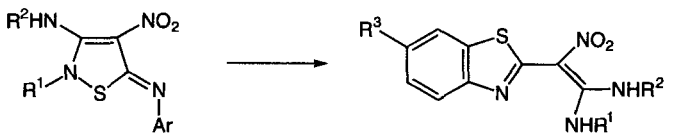
Table 2. *Selected Bond Lengths* [Å] *and Torsion Angles* [°] *of* **12e** (*cf. Fig. 1*)

S(1)–N(2)	1.726(2)	S(1)–C(5)	1.781(3)	N(2)–C(3)	1.345(3)
N(2)–C(6)	1.442(3)	C(3)–C(4)	1.428(3)	C(3)–N(19)	1.335(3)
C(4)–C(5)	1.440(3)	C(4)–N(18)	1.392(3)	C(5)–N(12)	1.282(3)
N(12)–C(13)	1.405(3)				
N(2)–C(3)–N(19)–C(20)		3.4(5)	C(4)–C(3)–N(19)–C(20)		–176.4(3)
C(3)–C(4)–N(18)–O(3)		–1.7(4)	C(3)–C(4)–N(18)–O(4)		178.7(2)
C(5)–C(4)–N(18)–O(3)		–179.1(2)	C(5)–C(4)–N(18)–O(4)		1.3(4)
C(4)–C(5)–N(12)–C(13)		172.8(3)	S(1)–C(5)–N(12)–C(13)		–9.4(4)

The bond lengths show that the π-systems are delocalized: the C(3)–C(4) bond (1.428(3) Å) is slightly longer than the delocalized C–C bonds in benzene and is, therefore, too long to be considered a formal double bond, and the C(4)–C(5) bond is significantly shorter than a C–C single bond. The N(2)–C(3), N(19)–C(3), and N(18)–C(4) bonds are also short and show a certain double-bond character (*cf. Table 2*). Thus, they must be involved in a delocalized π-bonding system. The conjugation of the lone electron pairs of N(2) and N(19) is also reflected by the planarity of these N-atoms. None of the phenyl-ring π-systems are interacting with that of the five-membered ring because the angles between the planes of the phenyl rings and that of the five-membered ring range from 62–70°. In summary, the bond system of **12e** may be resonably described as a completely delocalized π-system (*cf. Fig. 1*).

2.2. *Isomerization of* **12** *to 2-(Benzothiazol-2-yl)-2-nitroethene-1,1-diamines* **13** (*Scheme 4*). Surprisingly, **12a** rearranged into an isomeric compound during NMR

Scheme 4[a])



12 **13**

[a]) For R^1, R^2, R^3, and Ar, see *Table 1*.

measurements in (D_6)DMSO at room temperature. The ^{1}H-NMR spectra exhibited the appearence of downfield-shifted signals for some aromatic H-atoms and NH; the intensity of the new signals increased at the expense of those originally appearing. After 24 h, the spectrum displayed a broad *s* for two NH at 11.75 ppm (shifted by *ca.* 0.75 ppm) and two *d* ($J = 9.5$) at 7.87 and 7.69 ppm, each for one aromatic H-atom, as the most significant changes[4]). The ^{13}C-NMR spectra showed a pronounced broadening and shifting of the signals over time, which made their assignment difficult and confirmed the transformation of **12a** into a different compound. We assumed that the new product was a more stable tautomer of **12a**, but all attempts to establish the structure by means of spectral data failed. After crystallization from EtOH it was shown by X-ray crystallography that the new product was 2-(benzothiazol-2-yl)-2-nitroethene-1,1-diamine **13a** (*Fig. 2*).

Each amino group of the molecule forms an intramolecular H-bond, one with an O-atom of the NO_2 group (N ··· O 2.525(3) Å, N–H ··· O 150(3)°) and the other with the

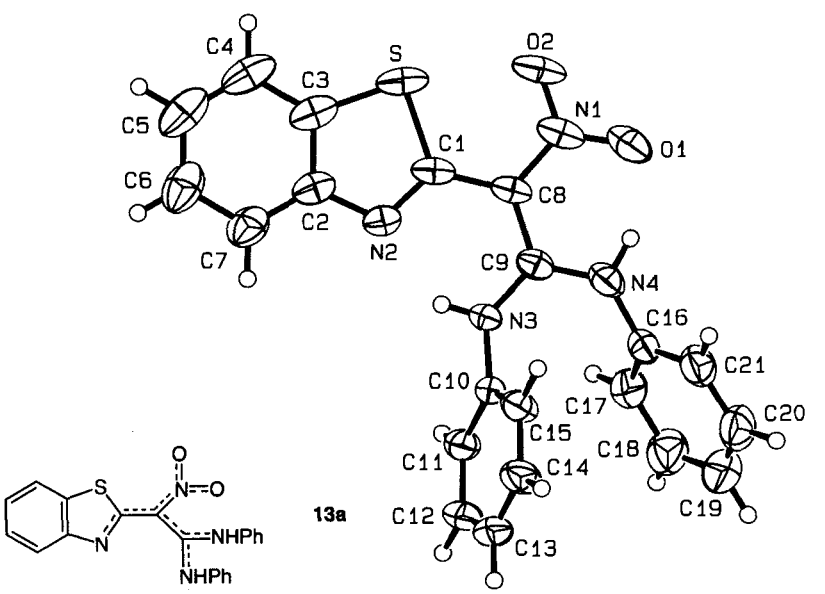


Fig. 2. *ORTEP Plot* [34] *of the molecular structure of* **13a** (arbitrary numbering of the atoms, with 40% probability ellipsoids)

[4]) The corresponding chemical shifts for **13a** in CD_2Cl_2 (*cf. Exper. Part*) are 14.04, 7.92, and 7.81 ppm.

N-atom of the thiazole ring (N ··· N 2.591(4) Å, N–H ··· N 142(3)°). These H-bonds complete two additional rings within the molecule. There are no intermolecular H-bonding interactions. With the exception of the two Ph groups, the molecule is planar; the mean deviation of all atoms from the plane is 0.024 Å. The amino N-atoms show the greatest deviation from the plane (0.07 and 0.10 Å) because of a small twist (*ca.* 5°) about the C(8)–C(9) bond [5]. The bond lengths of the C–C and C–N bonds in the chain from C(1) to N(3) and N(4), and including the NO_2 group, indicate considerable bond delocalization (*cf. Table 3*).

As established for **12a**, the 2-aryl-substituted isothiazole derivatives **12a–g** undergo a spontaneous isomerization in DMSO to give 2-(benzothiazol-2-yl)-2-nitroethene-1,1-diamines **13a–g**. The solvent dependence of this transformation was established by ^{1}H-NMR spectroscopy. The rate of isomerization was found to depend on the polarity of the solvent, occurring rapidly in DMSO, slower in acetone, but not at all in CH_2Cl_2. Therefore, the ^{1}H-NMR characterization of both isomers was performed in CD_2Cl_2 solution, in which no transformation takes place.

Whereas, *e.g.* **12a** exihibits in CD_2Cl_2 only a *m* for all 15 aromatic H-atoms and a *s* for one NH, **13a** shows at low field 2*d* and 2*t*, assigned to the 4 H-atoms of the benzothiazole ring, in addition to a *m* for 10 aromatic H-atoms, and a significantly downfield-shifted *s* for 2 NH. Signal assignment was achieved using one-bond coupling constants and ^{1}H,^{1}H correlation (COSY) spectra. ^{13}C-NMR spectroscopy also confirms the structure of each compound, the spectra displaying significant differences in the aromatic region. As expected, signals for 15 aromatic CH and 3 quaternary C-atoms are observed in the spectrum of **12a**, while for **13a**, signals for 14 aromatic CH and 4 quaternary C-atoms are present.

To evaluate the influence of electron-donating and -withdrawing substituents on the reaction rate, **12a–g** were dissolved in (D_6)DMSO at room temperature, and the isomerization was monitored by means of ^{1}H-NMR spectroscopy and TLC. The results of these studies are summarized in an isomerization rate/time diagram (*Fig. 3*). The diagram shows that an electron-withdrawing substituent in the 4-position of the Ar substituent of the arylimino group (see **12e**), as well as an electron-donating group in the 4-position of the phenyl ring at N(2) (R^1) and the amino group at C(3) (R^3) of the isothiazol ring (see **12b**), retarded the reaction. A similar effect was observed with the 3-methylamino derivative **12f**. In contrast, an electron-donating substituent in the Ar substituent of the arylimino group (see **12d**) and an electron-withdrawing substituent in the phenyl ring at N(2) or the phenylamino group at C(3) (see **12c**) caused the opposite effect, and a faster transformation took place.

Table 3. *Selected Bond Lengths* [Å] *and Torsion Angles* [°] *of* **13a** (*cf. Fig. 2*)

S–C(1)	1.755(3)	C(1)–N(2)	1.306(3)	C(1)–C(8)	1.457(4)
N(1)–C(8)	1.385(4)	C(8)–C(9)	1.439(4)	N(3)–C(9)	1.328(4)
N(4)–C(9)	1.339(4)				

S–C(1)–C(8)–N(1)	–0.3(4)	S–C(1)–C(8)–C(9)	178.8(2)
N(1)–C(8)–C(1)–N(2)	179.4(3)	N(2)–C(1)–C(8)–C(9)	–1.5(5)
C(1)–C(8)–N(1)–O(1)	178.0(3)	C(1)–C(8)–N(1)–O(2)	–2.0(4)
C(1)–C(8)–C(9)–N(3)	4.6(4)	C(1)–C(8)–C(9)–N(4)	–175.1(3)
C(8)–C(9)–N(3)–C(10)	–157.5(3)	C(8)–C(9)–N(4)–C(16)	–164.7(3)

[5]) The arbitrary numbering of the atoms in the ORTEP diagram (*Fig. 2*) is used.

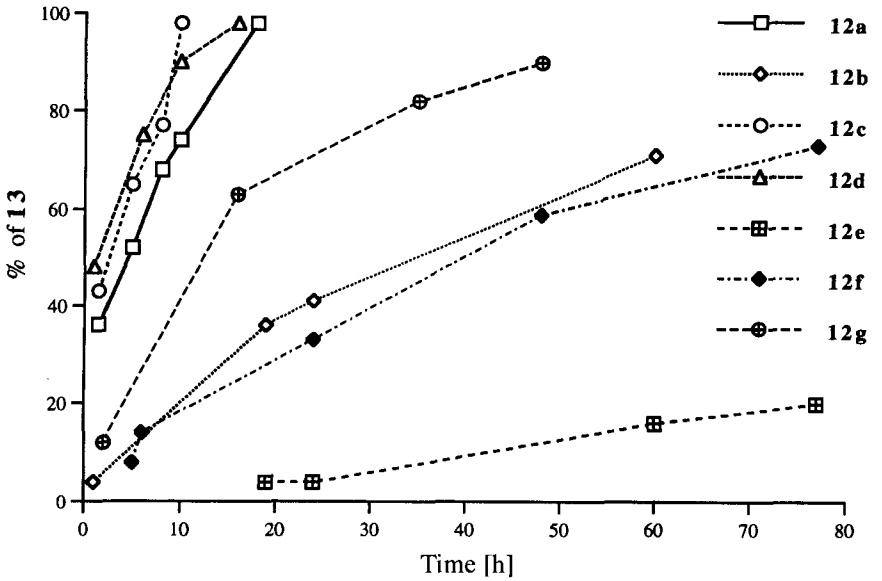


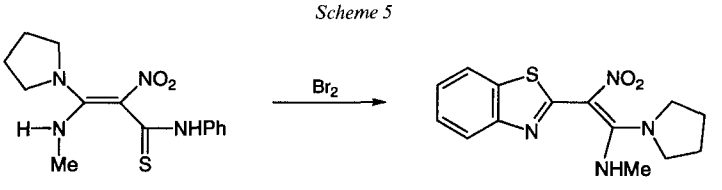
Fig. 3. *Isomerization rate of* **12a–g** *(cf. Table 1) in (D$_6$)DMSO at room temperature*

Thus, **12c** and **12d**, as well as the parent compound **12a**, isomerized by *ca.* 40% when the solutions were prepared at room temperature. On the other hand, the N(2)-alkyl-substituted isothiazoles **12h–k** remained unchanged in DMSO at room temperature, even after longer reaction times. The corresponding isomerization to **13h–k** was observed when (D$_6$)DMSO solutions were heated to 80°.

Although, according to ^{1}H-NMR spectra, the transformations of **12** to **13** were quantitative (either at room temperature or at 80°), the yield of isolated **13** was only 56–96% (*Table 1*).

2.3. *Synthesis of α-[(Benzothiazol-2-yl)nitromethylidene]-*N*-methylpyrrolidine-1-methanamine* (**13l**). Compound **13l** was prepared, as previously reported [20], *via* an oxidative cyclization of 3-(methylamino)-2-nitro-*N*-phenyl-3-(pyrrolidin-1-yl)thioacrylamide (**11l**) using Br_2 as the reagent (*Scheme 5*). Taking into account the above-mentioned results, we considered the possibility that, in this case, an isothiazole derivative of type **12** might also have been formed, which underwent a spontaneous isomerization to **13l** on recrystallizing from MeOH. The analysis of the crude reaction product by means of spectral data confirmed the structure reported by *Rajappa et al.*, and no **12l** could be detected. All attempts to reproduce the cyclization using DEAD [31] under the condi-

Scheme 5



11l **13l**

tions described in *Sect. 2.1*, instead of Br_2, lead to undefined products in an intractable mixture.

As **111** showed an uncommon behavior towards Br_2 and DEAD, the structure of this compound was studied by X-ray crystallography and NMR analysis. Interestingly, the X-ray analysis of **111** revealed that the pyrrolidine ring is disordered with two distinct conformations having the relative populations 0.866:0.134 (*Fig. 4,a*). Resolution of the disorder was achieved by defining two positions for C(11) and C(12)[6]). The two confor-

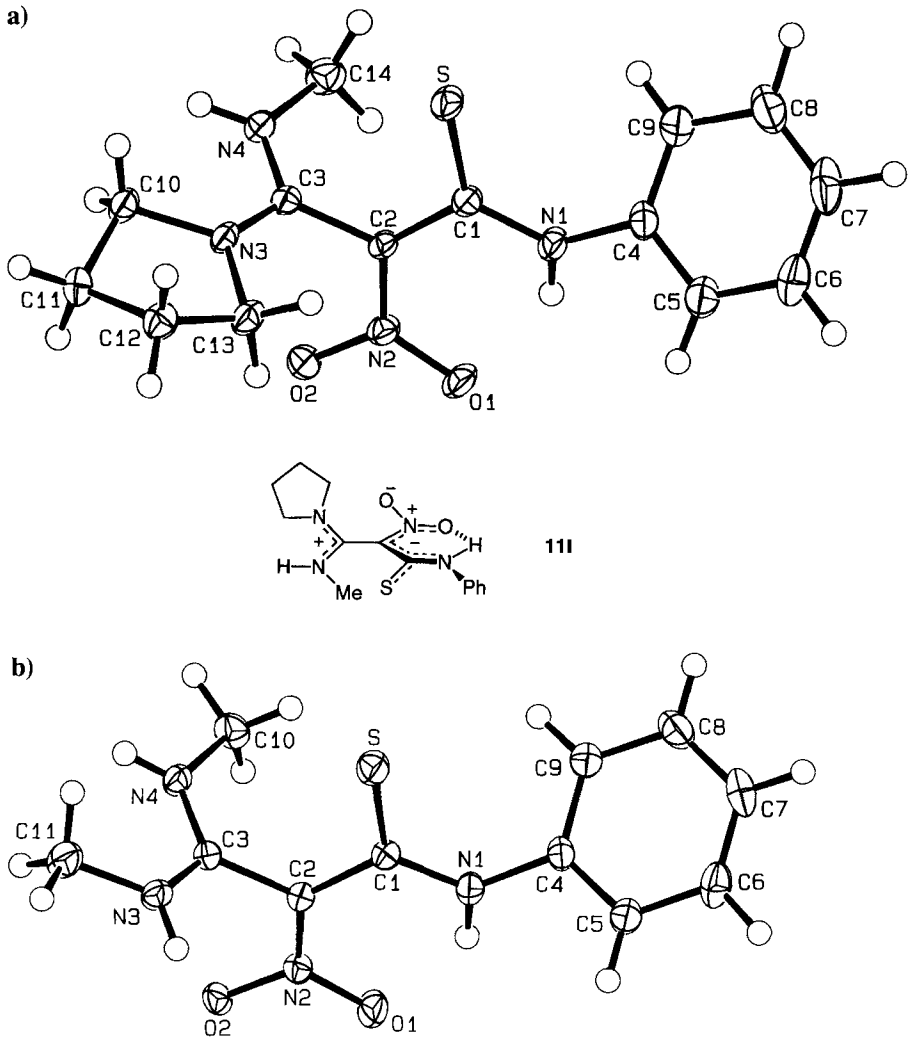


Fig. 4. *ORTEP Plots* [34] *of the molecular structures of* a) **111** *and* b) **11k** (arbitrary numbering of the atoms, with 50% probability ellipsoids; only the main conformation of **111** is shown)

[6]) The arbitrary numbering of the atoms in the ORTEP diagram (*Fig. 4*) is used.

mations represent reverse orientations of a half-chair conformation in which C(11) and C(12) lie on opposite sides of the plane formed by N(3), C(10), and C(13). Furthermore, the C(2)–C(3) bond (1.487(3) Å) is almost long enough to be considered a single bond, and the torsion angles about it have a mean value of 78°. Thus, this bond cannot be described as a double bond, and there is little likelihood of significant π-orbital overlap. The C(1)–C(2), N(2)–C(2), N(3)–C(3), N(4)–C(3), and N(1)–C(1) bonds are all considerably shorter than normal single bonds (*cf. Table 4*), so that independent delocalized bonding systems probably exist at each end of the C(2)–C(3) bond. A zwitterionic structure would account for these observations (*cf. Fig. 4a*). The NH of the thioamide group forms an intramolecular H-bond with one of the O-atoms of the NO_2 group (N ··· O 2.612(3) Å, N–H ··· O 140(3)°), forming a 6-membered ring, while the other NH group is involved in an intermolecular H-bond with the other O-atom of the NO_2 group (N ··· O 2.869(3) Å, N–H ··· O 147(3)°) of a neighboring molecule. The intermolecular H-bond links the molecules into infinite one-dimensional chains running parallel to the *y*-axis.

The crystal structure of **11k** was also determined (*Fig. 4, b*) and is very similar to that of **11l** (*Fig. 4, a*). The C(2)–C(3) bond (1.491(2) Å) is again almost a single bond, and the torsion angles about it have a mean value of 83°, suggesting another zwitterionic structure. The molecule has three planar regions, the five atoms of the two amino groups (N(3), N(4), C(3), C(10), C(11), mean deviation 0.01 Å), the main chain with N(1), C(1), C(2), and C(4), including the S-atom and the NO_2 group (mean deviation 0.02 Å), and

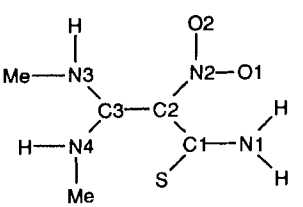
Table 4. *Selected Bond Lengths* [Å] *and Torsion Angles* [°] *of* **11l** *and* **11k** (*cf. Fig. 4*)

11l				**11k**			
S–C(1)	1.686(3)	N(1)–C(1)	1.345(3)	S–C(1)	1.683(2)	N(1)–C(1)	1.347(2)
C(1)–C(2)	1.446(3)	N(2)–C(2)	1.360(3)	C(1)–C(2)	1.447(2)	N(2)–C(2)	1.346(2)
C(2)–C(3)	1.487(3)	N(3)–C(3)	1.315(3)	C(2)–C(3)	1.491(2)	N(3)–C(3)	1.314(2)
N(4)–C(3)	1.327(3)			N(4)–C(3)	1.322(2)		
S–C(1)–N(1)–C(4)			1.7(4)	S–C(1)–N(1)–C(4)			2.8(2)
C(2)–C(1)–N(1)–C(4)			−174.9(3)	C(2)–C(1)–N(1)–C(4)			−178.0(1)
N(1)–C(1)–C(2)–C(3)			−179.1(2)	N(1)–C(1)–C(2)–C(3)			174.9(1)
N(1)–C(1)–C(2)–N(2)			5.8(4)	N(1)–C(1)–C(2)–N(2)			−1.9(2)
S–C(1)–C(2)–C(3)			3.9(3)	S–C(1)–C(2)–C(3)			−5.8(2)
S–C(1)–C(2)–N(2)			−171.1(2)	S–C(1)–C(2)–N(2)			177.4(1)
O(1)–N(2)–C(2)–C(1)			−0.5(4)	O(1)–N(2)–C(2)–C(1)			−1.0(2)
O(1)–N(2)–C(2)–C(3)			−175.8(2)	O(1)–N(2)–C(2)–C(3)			−177.9(1)
O(2)–N(2)–C(2)–C(1)			178.5(2)	O(2)–N(2)–C(2)–C(1)			180.0(1)
O(2)–N(2)–C(2)–C(3)			3.2(3)	O(2)–N(2)–C(2)–C(3)			3.0(2)
C(1)–C(2)–C(3)–N(3)			−101.2(3)	C(1)–C(2)–C(3)–N(3)			99.3(2)
C(1)–C(2)–C(3)–N(4)			81.4(3)	C(1)–C(2)–C(3)–N(4)			−81.8(2)
C(2)–C(3)–N(4)–C(14)			−7.1(4)	C(2)–C(3)–N(4)–C(10)			3.2(2)
C(2)–C(3)–N(3)–C(10)			−174.1(2)	C(2)–C(3)–N(3)–C(11)			179.6(2)
C(2)–C(3)–N(3)–C(13)			4.0(4)	–			
N(2)–C(2)–C(3)–N(3)			74.3(3)	N(2)–C(2)–C(3)–N(3)			−83.5(2)
N(2)–C(2)–C(3)–N(4)			−103.0(3)	N(2)–C(2)–C(3)–N(4)			95.4(2)
N(3)–C(3)–N(4)–C(14)			175.6(2)	N(3)–C(3)–N(4)–C(10)			−177.9(2)
N(4)–C(3)–N(3)–C(10)			3.2(4)	N(4)–C(3)–N(3)–C(11)			0.7(3)

the phenyl ring. The dihedral angle between the least-squares plane of the two MeN groups and that of the main chain is 83° (*cf.* above), and the plane of the phenyl ring makes an angle of 58° with that of the main chain. The molecules form two intermolecular and one intramolecular H-bonds. Each of the MeNH groups forms an intermolecular H-bond with O(2) of the NO_2 group of two different neighboring molecules; O(2), therefore, accepts two H-bonds (N···O 2.812(2) and 2.921(2) Å, N–H···O 164(2) and 159(2)°, resp.). One of these interactions links the molecules into infinite one-dimensional chains running parallel to the *z*-axis, the other links pairs of molecules into centrosymmetric dimers, which cross-link the one-dimensional chains in the *y*-direction. Thus, the combination of intermolecular interactions links the molecules into infinite two-dimensional networks which lie parallel to the *xz*-plane. The NH of the thioamide group forms an intramolecular H-bond with O(1) of the NO_2 group (N···O 2.626(2) Å, N–H···O 138(2)°), thus forming a 6-membered ring.

The ^{1}H-NMR spectra of **11l** showed nonequivalent CH_2N groups in the pyrrolidinyl residue, suggesting a significant barrier to free rotation around the N(3)–C(3) bond (*Fig. 4, a*). Coalescence of the CH_2N signals occurred upon warming to 90°. It is also interesting to note that this N–C rotation barrier implies a partial double-bond character for the N(3)–C(3) bond and, as a result, a decrease in the C(2)–C(3) double-bond character. This solution behavior is, therefore, analogous to the solid-state structure of the molecule. Attempts to confirm this by means of NOE spectra led to NOE exchange cross-peaks of N(4)H to CH_2N, but no NOE of Me to CH_2N could be observed, pointing to an additional N(4)–C(3) rotation barrier. All these data support the zwitterionic structure shown in *Fig. 4, a*.

A calculation of the molecular structure of **11m** with the GAMESS program (6–31 G* values) [35] yielded bond lengths and torsion angles which were very similar to those in the solid-state structures of **11k** and **11l**. In addition, the bond orders and charge distribution within the calculated structure of **11m** support the delocalized zwitterionic structure depicted in *Fig. 4a*. Details of these calculations will be reported later [36].



11m

S-C(1)	1.712	O(2)-N(2)	1.217
N(1)-C(1)	1.324	C(2)-C(3)	1.482
C(1)-C(2)	1.418	N(3)-C(3)	1.309
N(2)-C(2)	1.378	N(4)-C(3)	1.315
O(1)-N(2)	1.212		
C(1)-C(2)-C(3)-N(4)	78.9°		

Selected calculated bond lengths [Å]

3. Discussion. – As previously reported by *Rajappa et al.*, 3,3-diamino-2-nitrothioacrylamides of type **3** and **11** were cyclized with Br_2 affording 3-amino-4-nitroisothiazol-5(2*H*)-imines [19] [20]. The yields of this synthesis were only modest, presumably because of side reactions of Br_2 with the unsaturated system. By using DEAD, a well known dehydrogenation reagent [32] [33], we could avoid these undesired side reactions, and after an easy isolation, the products of type **12** were obtained in high yields. How-

ever, the scope of this synthesis is severely limited to 3,3-diamino-2-nitrothioacrylamides bearing two NH groups at C(3). Unsymmetrical derivatives with one NH and one disubstituted amino group, *e.g.*, 3-(methylamino)-2-nitro-*N*-phenyl-3-(pyrrolidin-1-yl)-thioacrylamide (**11l**), react with Br_2 to give 2-(benzothiazol-2-yl)-2-nitroethene-1,1-diamines **13**, instead of the expected isothiazol-5(2*H*)-imines **12** (*cf.* [20])[7]). In contrast, no reaction was observed with DEAD as the reagent.

We assumed that, in the case of **11l**, the corresponding isothiazol-5(2*H*)-imine could not be formed because of unfavorable steric interactions between the S-atom and the MeNH group at C(3) as well as between the pyrrolidine ring and the NO_2 group (*cf. Fig. 4a*). Since **11a–k**, which all yielded derivatives of type **12**, possess two monosubstituted amino groups at C(3), one of the two N-atoms should lie, in solution, in a favorable position with respect to the S-atom, thus allowing the nucleophilic attack. However, comparison of the crystal structures of **11k** and **11l** (*Fig. 4*) does not give any unambiguous indication for such a difference. Furthermore, the fact that 2-(benzothiazol-2-yl)-2-nitroethene-1,1-diamine formation was not achieved by using DEAD suggests different reaction mechanisms for the two reactions.

To the best of our knowledge, there is no precedent for an isomerization of type **12**→**13**. Taking into account that the reaction was observed only in polar solvents, a mechanism involving ring opening of the heterocycle leading to a zwitterion **A** is proposed in *Scheme 6*. Supposing that this ring opening of **12** is the rate-determining step, the observed influence of the substituents is easily understandable: electron-withdrawing substituents R^1 as well as electron-donating substituents Ar stabilize the ionic intermediate **A** by conjugation (*cf.* **A′** and **A″**, resp.), and, therefore, they can reduce the activation energy of the ring opening. Electron-donating substituents R^1 and electron-withdrawing arylimino groups have the opposite effect.

Formally, the ring closure to the 2-(benzothiazol-2-yl)-2-nitroethene-1,1-diamine **13** can be interpreted by two different mechanisms. Formula **A′** suggests an electrophilic aromatic substitution of the arylimino moiety by the electrophilic S-atom to give **B**, which aromatizes to yield **13**. On the other hand, a nucleophilic attack of the S-atom onto the arylimino group leading to **C** is reasonable according to formula **A″**. This mechanism should be favored when Ar bears an electron-donating group in the 4-position.

The remarkable influence of substituents on the reported isomerization is also confirmed by the fact that isothiazoles **12** with an alkyl group at N(2) isomerize only at higher temperatures. It seems that in these cases the polarity of the solvents is not sufficient for a spontaneous bond cleavage, and heating is necessary for the transformation into the thermodynamically more stable **13**.

We thank especially Mr. *M. Binder* for NMR spectra and helpful discussions concerning the elucidation of possible conformations of compounds **11l**, **12a**, and **13a**. We thank also Mr. *L. Bigler* and Dr. *E. Reder* for mass spectra, and Dr. *R. W. Kunz* for performing the calculation of **11m**. Financial support of this work by the *Schweizerische Eidgenössische Stipendienkommission* and *F. Hoffmann-La Roche AG*, Basel, is gratefully acknowledged.

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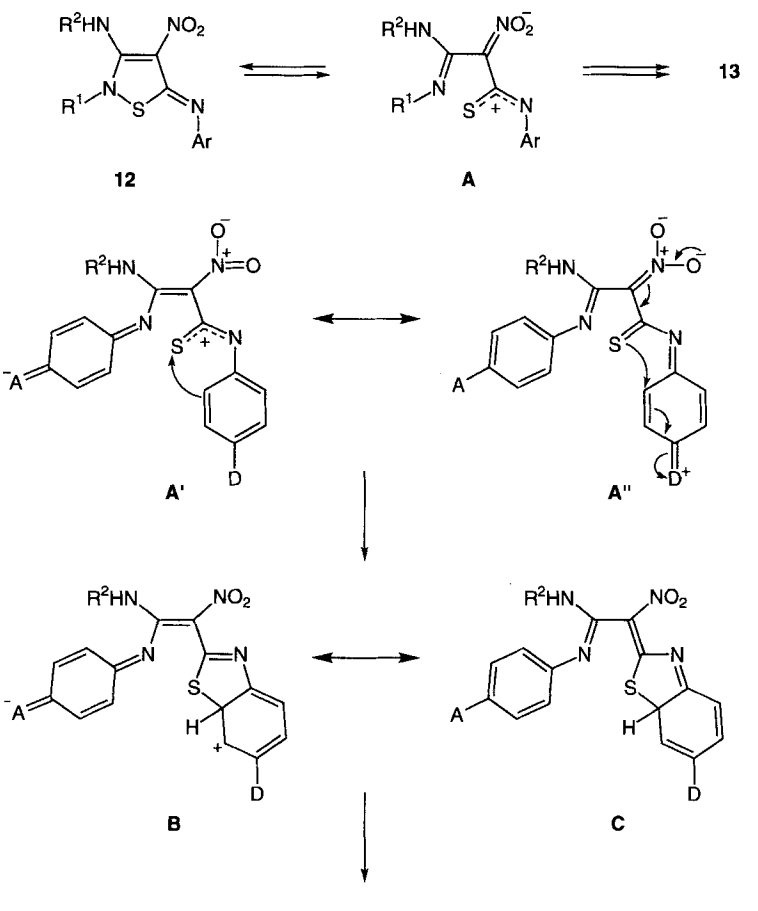
[7]) The synthesis of benzothiazoles starting from thioamides is well documented. Suitable reagents for this purpose are NaH/DMF in toluene [37], *t*-BuOK and Na_2CO_3 in DMF [38], $NaNH_2$ in liquid NH_3 [39], $K_3[Fe(CN)_6]$ in H_2O [40], and Br_2 in AcOH [41] or in $CHCl_3$ [42].

Scheme 6



Experimental Part

1. *General.* See [27]. The starting 2-nitroethene-1,1-diamines were synthesized according to the general procedures described in [17] [29] [30]. An improved synthesis of the 3,3-diamino-2-nitrothioacrylamides (= 3,3-diamino-2-nitroprop-2-enethioamides) **11** has already been reported by us [24]. IR Spectra: in KBr. ^{1}H- and ^{13}C-NMR Spectra: *Bruker-ARX-300* instrument at 300 MHz; in (D_6)DMSO, unless otherwise stated. EI- and CI-MS (NH_3 as ionization gas): *Finnigan-SSQ-700* or *-MAT-90* instrument; ESI mode on *Finnigan-TSQ-700* triple-quadrupole spectrometer.

2. *3,3-Diamino-2-nitrothioacrylamides* **11**. *2-Nitro*-N,N'-*diphenylethene-1,1-diamine. Cf.* [30].

N,N'-*Bis(4-methoxyphenyl)-2-nitroethene-1,1-diamine.* Recrystallized from MeOH: 14.6 g (93%). Yellow crystals. M.p. 179–181°. IR: 3190 (br.), 2950*w*, 2830*w*, 1615*s*, 1595*s*, 1565*s*, 1510*s*, 1460*m*, 1440*m*, 1420*m*, 1390 (sh), 1355*s*, 1300*m*, 1265 (sh), 1240*s*, 1225 (sh), 1195*s*, 1180*s*, 1110*m*, 1045*s*, 1035 (sh), 980*m*, 860*m*, 850*m*, 770*m*, 760*m*, 700*w*. ^{1}H-NMR: 10.20 (br. *s*, 2 NH); 7.25, 6.97 (*AA'BB'*, 8 arom. H); 6.12 (*s*, CH); 3.76 (*s*, 2 MeO). ^{13}C-NMR: 158.3 (*s*, $(MeOC_6H_4NH)_2C$=); 155.4 (*s*, 2 arom. C); 128.9 (*s*, 2 arom. C); 127.6, 115.0 (2*d*, 8 arom. CH); 99.8 (*d*, CH); 55.7 (*q*, 2 MeO). CI-MS: 316 (26, $[M+1]^+$), 124 (100). Anal. calc. for $C_{16}H_{17}N_3O_4$ (315.33): C 60.94, H 5.43, N 13.33; found: C 60.91, H 5.46, N 13.40.

N,N'-*Bis(4-fluorophenyl)-2-nitroethene-1,1-diamine.* Recrystallized from MeOH: 13.7 g (94%). Yellow crystals. M.p. 172–174°. IR: 3430 (br.), 3190*m*, 3160*m*, 3060*m*, 3040*m*, 1620*s*, 1598*s*, 1565*s*, 1510*s*, 1480*m*, 1470*m*,

1435*m*, 1415*s*, 1400*s*, 1365 (br.), 1300*m*, 1290*m*, 1260*s*, 1225*s*, 1190*s*, 1155*s*, 1105*m*, 1095*m*, 1040*s*, 985*s*, 860*m*, 845*m*, 830 (sh), 808*m*, 780*m*, 760*s*, 705*m*. ^{1}H-NMR: 10.27 (br. *s*, 2 NH); 7.4–7.3 (*m*, 4 arom. H); 7.25–7.2 (*m*, 4 arom. H); 6.21 (*s*, CH). ^{13}C-NMR: 160.7 (*d*, ^1J(C,F) = 245.0, 2 arom. C); 154.8 (*s*, $(FC_6H_4NH)_2C$=); 133.0 (*s*, 2 arom. C); 127.8 (*dd*, ^3J(C,F) = 8.9, 4 arom. CH); 116.5 (*dd*, ^2J(C,F) = 23.0, 4 arom. CH); 100.5 (*d*, CH). ESI-MS: 314 ($[M + Na]^+$).

N-*Methyl-2-nitro*-N′-*phenylethene-1,1-diamine*. Recrystallized from MeOH: 8.5 g (88%). White crystals. M.p. 179–181°. IR: 3250 (sh), 3200*m*, 3100*m*, 3045*m*, 2975*m*, 1695*w*, 1660 (sh), 1645*s*, 1635*s*, 1600*m*, 1590*m*, 1565 (sh), 1555*s*, 1540 (sh), 1505 (sh), 1495*m*, 1485*m*, 1465*m*, 1455*s*, 1445*m*, 1435 (sh), 1430*s*, 1405*s*, 1375*s*, 1325 (sh), 1250*s*, 1220*s*, 1200 (sh), 1155*m*, 1100*m*, 1075*m*, 1035*s*, 1000*m*, 990*m*, 940*m*, 905*m*, 855*w*, 765*m*, 750*m*, 730*s*, 700*s*, 665*m*. ^{1}H-NMR: 10.01, 9.09 (2 br. *s*, 2 NH); 7.5–7.2 (*m*, 5 arom. H), 6.12 (br. *s*, CH); 2.98 (br. *s*, *Me*NH). ^{13}C-NMR: 155.9 (*s*, (MeNH)(PhNH)*C*=); 136.4 (*s*, 1 arom. C); 129.4, 126.7, 126.0 (3 *d*, 5 arom. CH); 98.3 (*d*, CH); 28.5 (*q*, Me). ESI-MS: 216 ($[M + Na]^+$).

N,N′-*Dibenzyl-2-nitroethene-1,1-diamine*. *Cf.* [17].

N,N′-*Dimethyl-2-nitroethene-1,1-diamine*. *Cf.* [17].

2-Nitro-N-*phenyl-3,3-bis(phenylamino)prop-2-enethioamide* (**11a**). *Cf.* [24].

3,3-Bis[(4-methoxyphenyl)amino]-2-nitro-N-*phenylprop-2-enethioamide* (**11b**). Chromatography (CH_2Cl_2/MeOH): 1.0 g (59%). Yellow powder. M.p. 145–146°. IR: 3440 (br.), 3180 (br.), 2940*m*, 2830*m*, 1635*s*, 1595 (br.), 1588*m*, 1510*s*, 1465 (sh), 1425*s*, 1410*s*, 1350*s*, 1300*s*, 1250*s*, 1215*m*, 1180 (sh), 1168*m*, 1110 (sh), 1095*m*, 1030*s*, 1010 (sh), 945*s*, 905*w*, 835*m*, 810*m*, 785 (sh), 765*m*, 698*m*. ^{1}H-NMR: 13.13 (*s*, PhN*H*); 10.78 (br. *s*, 2 NH); 7.68 (br. *s*, 2 arom. H); 7.4–7.25 (*m*, 6 arom. H); 7.12 (*t*, *J* = 7.4, 1 arom. H); 6.95 (*d*, *J* = 8.9, 4 arom. H); 3.75 (*s*, 2 MeO). ^{13}C-NMR: 179.7 (*s*, C=S); 158.9 (*s*, $(MeOC_6H_4NH)_2C$=); 158.4, 139.1, 128.7 (3*s*, 5 arom. C); 128.4, 125.6, 124.9, 122.7 (4 *d*, 11 arom. CH); 115.9 (*s*, $=CNO_2$); 113.4 (br. *d*, 2 arom. CH); 55.2 (*q*, 2 MeO). ESI-MS: 473 ($[M + Na]^+$), 449 ($[M - 1]^+$).

3,3-Bis[(4-fluorophenyl)amino]-2-nitro-N-*phenylprop-2-enethioamide* (**11c**). Recrystallized from MeOH: 0.8 g (53%). Yellow crystals. M.p. 160–162°. IR: 3440 (br.), 3200*m*, 3060 (br.), 2940 (br.), 1640*s*, 1600*s*, 1540 (br.), 1505*s*, 1465 (sh), 1445 (sh), 1430 (sh), 1420*s*, 1385 (sh), 1360 (br.) 1290*s*, 1238*s*, 1208*s*, 1155*m*, 1110*m*, 1100*m*, 1090*m*, 1030*w*, 1015*w*, 945*s*, 900*m*, 840*s*, 810*m*, 795*m*, 785*m*, 755*m*, 750 (sh), 715*m*, 695*m*. ^{1}H-NMR (600 MHz; *Bruker AMX-600*): 13.12 (*s*, PhN*H*); 11.39 (br. *s*, 2 NH); 7.72 (br. *s*, 2 arom. H); 7.75–7.15 (*m*, 11 arom. H). ^{13}C-NMR (600 MHz; *Bruker AMX-600*): 179.6 (*s*, C=S); 160.5 (*d*, ^1J(C,F) = 245.0, 2 arom. C); 160.2 (*s*, $(FC_6H_4NH)_2C$=); 138.8 (*s*, 1 arom. C); 132.3 (*d*, ^4J(C,F) = 2.8, 2 arom. C); 128.5, 125.0, 122.9 (3*d*, 5 arom. CH); 126.4 (*dd*, ^3J(C,F) = 8.9, 4 arom. CH); 116.0 (*dd*, ^2J(C,F) = 23.0, 4 arom. CH); 115.5 (*s*, $=CNO_2$). ESI-MS: 449 ($[M + Na]^+$), 425 ($[M - 1]^+$).

N-*(4-Methoxyphenyl)-2-nitro-3,3-bis(phenylamino)prop-2-enethioamide* (**11d**). Chromatography (CH_2Cl_2/MeOH): 0.9 g (58%). Yellow crystals. M.p. 152–154°. IR: 3340 (br.), 3060*m*, 2980 (br.), 2920 (br.), 1715*m*, 1640*s*, 1615 (sh), 1585*s*, 1550*s*, 1510*s*, 1495*s*, 1465*s*, 1455 (sh), 1445*s*, 1425*s*, 1395*s*, 1370*s*, 1335 (sh), 1300*m*, 1250*s*, 1215*m*, 1175*m*, 1105*m*, 1095*m*, 1070*m*, 1030*m*, 1005*w*, 945*s*, 930*s*, 830*m*, 800*w*, 750*s*, 690*m*. ^{1}H-NMR: 13.02 (br. *s*, NH); 11.33 (br. *s*, 2 NH); 7.6–7.1 (*m*, 12 arom. H); 6.90 (br. *d*, 2 arom. H); 3.69 (*s*, MeO). ^{13}C-NMR: 180.1 (*s*, C=S); 158.8 (*s*, $(PhNH)_2C$=); 157.0, 136.5, 132.3 (3*s*, 4 arom. C); 129.5, 127.9, 125.1, 124.3, 114.0 (5 *d*, 14 arom. CH); 116.2 (*s*, $=CNO_2$); 55.6 (*q*, MeO). ESI-MS: 443 ($[M + Na]^+$), 419 ($[M - 1]^+$).

2-Nitro-N-*(4-nitrophenyl)-3,3-bis(phenylamino)prop-2-enethioamide* (**11e**). Chromatography (CH_2Cl_2/MeOH): 0.9 g (57%). Yellow crystals. M.p. 160–161°. IR: 3190 (br.), 3070 (br.), 1704*m*, 1645 (sh), 1635*s*, 1595 (sh), 1585*s*, 1565*s*, 1555*s*, 1515*s*, 1505*s*, 1495*s*, 1470*m*, 1455 (sh), 1445*s*, 1425 (br.), 1405 (br.), 1370 (br.), 1335*s*, 1310 (sh), 1285*s*, 1250*m*, 1210*m*, 1175*m*, 1155 (sh), 1112*m*, 1095*m*, 1072*w*, 1028*w*, 1003*w*, 945*s*, 910 (sh), 860 (sh), 850*m*, 803*m*, 755*m*, 690*m*. ^{1}H-NMR ($(CD_3)_2CO$): 13.58 (*s*, PhN*H*); 10.56 (*s*, 2 NH); 8.3–8.15 (*m*, 4 arom. H); 7.65–7.3 (*m*, 10 arom. H). ^{13}C-NMR: 181.4 (*s*, C=S); 161.6 (*s*, $(PhNH)_2C$=); 146.5, 144.4, 136.2 (3*s*, 4 arom. C); 130.5, 129.5, 125.7, 125.0 (5 *d*, 14 arom. CH); 117.6 (*s*, $=CNO_2$). ESI-MS: 458 ($[M + Na]^+$), 434 ($[M - 1]^+$).

(E/Z)-3-(Methylamino)-2-nitro-N-*phenyl-3-(phenylamino)prop-2-enethioamide* (**11f**/**11h**). 1.1 g (92%). Yellow crystals. M.p. 176–177°. IR: 3195*m*, 3185 (sh), 3080 (br.), 1645 (sh), 1635*s*, 1595 (sh), 1575*m*, 1555 (sh), 1550*s*, 1540*s*, 1498*m*, 1488*m*, 1470*m*, 1465*m*, 1455 (sh), 1445*s*, 1425*s*, 1385 (sh), 1370*s*, 1335*s*, 1310*s*, 1290*m*, 1280*m*, 1250*m*, 1212*m*, 1160*m*, 1125*m*, 1070*m*, 1028*m*, 1015*m*, 995*m*, 940*s*, 925 (sh), 903*m*, 840*w*, 812*w*, 780*m*, 765*m*, 750*m*, 710*m*, 688*m*. ^{1}H-NMR[8]): 13.38, 13.24 (2*s*, NHCS); 11.18, 10.48 (2 br. *s*, PhN*H*); 10.10 (br. *d*, MeN*H*); 8.97 (br. *s*, MeN*H*); 7.85–7.1 (*m*, 10 arom. H); 3.05 (*d*, *J* = 4.7, *Me*NH); 2.81 (br. *s*, *Me*NH). ^{13}C-NMR[8]): 180.0

[8]) Doubling of some signals as a result of the presence of two isomers.

(*s*, C=S); 16.05 (*s*, (MeNH)(PhNH)*C*=); 139.5, 136.8 (2*s*, 2 arom. C); 130.4, 129.0, 128.9, 128.8, 127.7, 25.5, 125.3, 124.7, 123.4, 123.2 (10*d*, 10 arom. CH); 116.4 (*s*, $=CNO_2$); 30.2 (*q*, Me). ESI-MS: 367 ($[M + K]^+$), 351 ($[M + Na]^+$), 327 ($[M - 1]^+$).

(E/Z)-N-(4-Methoxyphenyl)-3-(methylamino)-2-nitro-3-(phenylamino)prop-2-enethioamide (**11g/11i**). 1.0 g (77%). Yellow crystals. M.p. 167–169°. IR: 3290*w*, 3200*m*, 3080*m*, 2295 (br.), 2930*m*, 1645 (sh), 1635*s*, 1595*s*, 1580*m*, 1555*m*, 1540 (sh), 1515*s*, 1495*m*, 1465*m*, 1455 (sh), 1445*s*, 1430*s*, 1380 (sh), 1370*s*, 1338*s*, 1300*m*, 1250*s*, 1220*m*, 1775*m*, 1130*m*, 1070*w*, 1030*s*, 1015*m*, 940*s*, 925*s*, 835*m*, 790*w*, 750*w*, 730*w*, 705*m*, 685*w*. ^{1}H-NMR[8]): 13.18, 13.03 (2 *s*, NHCS); 11.12, 10.39 (2*s*, PhN*H*); 10.04 (br. *q*, MeN*H*); 8.99 (br. *s*, MeN*H*); 7.7–7.2 (*m*, 7 arom. H); 6.9–6.8 (*m*, 2 arom. H); 3.70, 3.67 (2*s*, MeOH); 3.04 (*d*, *J* = 5.0, MeN); 2.77 (br. *s*, MeN). ^{13}C-NMR[8]): 179.8, 179.2 (2*s*, C=S); 160.5, 160.2 (2*s*, (MeNH)(PhNH)*C*=); 157.0, 156.9, 136.9, 135.6, 132.5 (5*s*, 3 arom. C); 130.4, 129.0, 128.1, 127.7, 125.2, 125.0, 124.8, 124.7, 114.0, 113.9 (10*d*, 9 arom. CH); 116.0, 114.8 (2*s*, $=CNO_2$); 55.6 (*q*, MeO); 30.4, 30.2 (2*q*, MeN). ESI-MS: 381 ($[M + Na]^+$).

3,3-Bis(benzylamino)-2-nitro-N-phenylprop-2-enethioamide (**11j**). *Cf.* [24].

3,3-Bis(methylamino)-2-nitro-N-phenylprop-2-enethioamide (**11k**). *Cf.* [24].

3-(Methylamino)-2-nitro-N-phenyl-3-(pyrrolidin-1-yl)prop-2-enethioamide (**11l**). *Cf.* [20].

3. *3-Amino-4-nitroisothiazol-5(2H)-imines* **12**: *General Procedure* [31]. To a soln. of **11** (3.1 mmol) in DMF (6.2 ml), diethyl azodicarboxylate (3.3 mmol, 0.52 ml) was added. The mixture was stirred for *ca.* 1 h (TLC monitoring) and then poured into ice water[9]). The precipitated yellow solid was filtered, washed with H_2O, and dried *in vacuo* overnight. The isothiazol-5(2*H*)-imines **12** were obtained in pure form and needed no further purification.

N,2-Diphenyl-3-(phenylamino)-4-nitroisothiazol-5(2H)-imine (**12a**): 1.2 g (97%). Yellow powder. M.p. 204–205°. IR: 3440 (br.), 3060*w*, 1610*m*, 1575 (sh), 1515*s*, 1530*s*, 1495 (sh), 1485*m*, 1455*m*, 1435*s*, 1370*m*, 1305*m*, 1230*m*, 1210*m*, 1175*w*, 1090*m*, 1075*w*, 1025*w*, 920*w*, 780 *m*, 750*m*, 690*m*. ^{1}H-NMR (CD_2Cl_2): 11.18 (br. *s*, NH); 7.34 (*t*, *J* = 7.8, 2 arom. H); 7.25–6.9 (*m*, 13 arom. H). ^{13}C-NMR (CD_2Cl_2): 156.0 (*s*, C(3)); 154.6 (*s*, C(5)); 153.7, 139.1, 135.7 (3*s*, 3 arom. C); 130.2, 129.7, 129.3, 128.9, 127.0, 126.3, 125.4, 125.1, 120.0 (9*d*, 15 arom. CH); 115.3 (*s*, C(4)). CI-MS: 390 (20), 389 (100, $[M + H]^+$), 373 (57), 357 (29), 355 (32). Anal. calc. for $C_{21}H_{16}N_4O_2S$ (388.44): C64.93, H4.15, N14.42, S8.25; found: C64.89, H4.14, N14.62, S8.03.

2-(4-Methoxyphenyl)-3-[(4-methoxyphenyl)amino]-4-nitro-N-phenylisothiazol-5(2H)-imine (**12b**): 1.3 g (91%). Yellow crystals. M.p. 144–145°. IR: 3440 (br.), 3070*w*, 2835*w*, 1615*s*, 1590*s*, 1575*s*, 1540*m*, 1510*s*, 1490*m*, 1435*s*, 1420*s*, 1385*m*, 1315*m*, 1305*m*, 1250*s*, 1210 (sh), 1175*m*, 1105 (sh), 1095*w*, 1030*m*, 920*w*, 830*m*, 750*w*, 695*w*. ^{1}H-NMR (CD_2Cl_2): 11.06 (*s*, NH); 7.33 (*t*, *J* = 8.2, 2 arom. H); 7.11 (*t*, *J* = 7.7, 1 arom. H); 7.0–6.95 (*m*, 2 arom. H); 6.9–6.8 (*m*, 4 arom. H); 6.55 (*dd*, *J* = 9.0, 3.2, 4 arom. H); 3.66 (*s*, 2 MeO). ^{13}C-NMR (CD_2Cl_2): 162.1 (*s*, C(3)); 159.9, 158.8, 156.8 (3*s*, 3 arom. C); 154.9 (*s*, C(5)); 153.8, 131.5 (2*s*, 2 arom. C); 130.1, 128.4, 127.3, 125.3, 120.1, 114.8, 114.4 (7*d*, 13 arom. CH); (*s*, C(4))[10]); 55.9, 55.8 (2*q*, 2 MeO). EI-MS: 448 (14, $M^{+\cdot}$), 402 (19), 325 (34), 122 (100), 108 (80), 80 (27).

3-(4-Fluorophenyl)-3-[(4-fluorophenyl)amino]-4-nitro-N-phenylisothiazol-5(2H)-imine (**12c**): 1.2 g (95%). Yellow crystals. M.p. 211–213°. IR: 3420 (br.), 3060*w*, 2920*w*, 1615*s*, 1585 (sh), 1570*s*, 1525*m*, 1505*s*, 1485 (sh), 1438*s*, 1418*m*, 1375*m*, 1315*m*, 1305 (sh), 1228*s*, 1215*s*, 1155*m*, 1105*m*, 1085*m*, 1070*w*, 1010*w*, 920*w*, 835*m*, 860*w*, 770*m*, 755*m*, 735*w*, 700*w*. ^{1}H-NMR (CD_2Cl_2): 11.08 (br. *s*, NH); 7.23 (*t*, *J* = 7.2, 2 arom. H); 7.03 (*t*, *J* = 6.9, 1 arom. H); 7.0–6.85 (*m*, 6 arom. H); 6.8–6.65 (*m*, 4 arom. H). ^{13}C-NMR (CD_2Cl_2): 162.3, 161.4 (2*d*, ^1J(C,F) = 250.0, 2 arom. C); 157.0 (*s*, C(3)); 154.5 (*s*, C(5)); 135.5 (*s*, 1 arom. C); 135.0, 131.8 (2*d*, ^4J(C,F) = 3.0, 2 arom. C); 130.2 (*d*, 2 arom. CH); 129.0, 127.7 (2*dd*, ^3J(C,F) = 8.6, 4 arom. CH); 125.6, 120.0 (2*d*, 3 arom. CH); 116.9, 116.3 (2*dd*, ^2J(C,F) = 23.3, 4 arom. CH); 115.2 (*s*, C(4)). ESI-MS: 447 ($[M + Na]^+$), 425 ($[M + H]^+$).

N-(4-Methoxyphenyl)-4-nitro-2-phenyl-3-(phenylamino)isothiazol-5(2H)-imine (**12d**): 1.0 g (75%). Yellow powder. M.p. 193–195°[11]). IR: 3440 (br.), 3050*w*, 1615*s*, 1590*s*, 1575*s*, 1565 (sh), 1530*s*, 1505*s*, 1455*s*, 1435*s*, 1375*s*, 1315 (sh), 1305*m*, 1288*m*, 1245*s*, 1205*s*, 1180*m*, 1155*m*, 1105*w*, 1085*m*, 1070*m*, 1030*m*, 908*w*, 870*w*, 830*m*, 790*w*, 765*m*, 755*m*, 725*w*, 695*m*. ^{1}H-NMR (CD_2Cl_2): 11.01 (br. *s*, NH); 7.45–6.9 (*m*, 14 arom. H); 3.73 (*s*, MeO). ^{13}C-NMR (CD_2Cl_2): 156.9 (*s*, C(3)); 155.5 (*s*, C(5)); 153.8, 146.5, 139.4, 136.5 (4*s*, 4 arom. C); 129.6, 129.2, 128.7, 128.6, 126.2, 124.5, 121.0, 115.4 (8*d*, 14 arom. CH); 114.9 (*s*, C(4)). EI-MS: 419 (13), 418 (36, $M^{+\cdot}$), 373 (27), 372 (100), 371 (67), 356 (26), 207 (33), 206 (55), 93 (23), 77 (49).

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[9]) In some cases, **12** precipitated from the mixture and was directly filtered, washed with H_2O, and dried *in vacuo*.

[10]) The signal for C(4) is obscured by the CH signals.

[11]) At *ca.* 150°, a transformation of the crystals was observed.

*4-Nitro-*N*-(4-nitrophenyl)-2-phenyl-3-(phenylamino)isothiazol-5(2*H*)-imine* (**12e**): 1.1 g (84%). Yellow crystals. M.p. 187–189°. IR: 3440 (br.), 3165*w*, 3060*w*, 1615*s*, 1590*s*, 1570*s*, 1535*s*, 1505*s*, 1495*s*, 1485*s*, 1455*m*, 1435*s*, 1375*s*, 1340*s*, 1305*s*, 1240*s*, 1220*s*, 1165*m*, 1110*s*, 1090*s*, 1070*m*, 1030*w*, 975*m*, 965*m*, 865*w*, 860*m*, 855*m*, 830*w*, 760*s*, 755 (sh), 690*s*. ^{1}H-NMR (CD_2Cl_2): 11.11 (br. *s*, NH); 8.25–8.15 (*m*, 2 arom. H); 7.2–6.95 (*m*, 12 arom. H). ^{13}C-NMR (CD_2Cl_2): 158.9 (*s*, 1 arom. C); 156.2 (*s*, C(3)); 155.6 (*s*, C(5)); 145.1, 138.7, 135.6 (3*s*, 3 arom. C); 130.1, 129.6, 127.6, 126.6, 126.3, 125.5, 121.1 (7*d*, 14 arom. CH); 115.6 (*s*, C(4)). EI-MS: 434 (14), 433 (58, $M^{+\cdot}$), 387 (27), 220 (42), 195 (25), 194 (58), 180 (60), 134 (33), 119 (32), 93 (74), 91 (44), 90 (42), 77 (100).

*3-(Methylamino)-4-nitro-*N*,2-diphenylisothiazol-5(2*H*)-imine* (**12f**): Chromatography (hexane/AcOEt/CH_2Cl_2): 0.4 g (44%). Yellow crystals. M.p. 74–76°. IR: 3240*w*, 3070*w*, 3010*w*, 1790*w*, 1770*w*, 1740*w*, 1715*w*, 1730*w*, 1695*w*, 1660*w*, 1655 (sh), 1645 (sh), 1625 (sh), 1610*s*, 1580*s*, 1555 (sh), 1540*m*, 1515*s*, 1505*m*, 1490*s*, 1470*m*, 1432*s*, 1410*s*, 1370*s*, 1335*m*, 1290 (br.), 1272*m*, 1240 (sh), 1220 (sh), 1210*s*, 1185*m*, 1170*m*, 1162*m*, 1152*m*, 1115*s*, 1075*m*, 1070*m*, 1028 (sh), 1022*w*, 1000*m*, 945*w*, 915*m*, 910 (sh), 895*w*, 825*w*, 765*s*, 740*w*, 692*s*, 670*m*. ^{1}H-NMR (CD_2Cl_2): 9.78 (br. *s*, NH); 7.8–6.9 (*m*, 10 arom. H); 2.60 (br. *s*, MeN). ^{13}C-NMR (CD_2Cl_2): 159.5 (*s*, C(3)); 155.1 (*s*, C(5)); 153.7, 140.5 (2*s*, 2 arom. C); 130.6, 130.1, 129.9, 127.1, 125.3, 120.1 (6*d*, 10 arom. CH); 114.4 (*s*, C(4)); 32.3 (*q*, MeN). ESI-MS: 349 ($[M + Na]^+$), 327 ($[M + H]^+$).

N*-(4-Methoxyphenyl)-3-(methylamino)-4-nitro-2-phenylisothiazol-5(2*H*)-imine* (**12g**): Chromatography (hexane/AcOEt/CH_2Cl_2): 0.5 g (48%). Yellow crystals. M.p. 149–151°. IR: 3440 (br.), 3220 (br.), 2940*w*, 2900 (sh), 2830*w*, 1615*s*, 1595*s*, 1540*s*, 1500*s*, 1465*m*, 1455 (sh), 1428*s*, 1415*s*, 1372*s*, 1315*m*, 1300*m*, 1288*s*, 1272*m*, 1240*s*, 1225 (sh), 1115*m*, 1075*w*, 1035*m*, 1003*m*, 955*w*, 930*w*, 918 (sh), 910*m*, 855*w*, 840*m*, 810*w*, 758*s*, 745*m*, 730*m*, 695*m*. ^{1}H-NMR: 9.78 (br. *q*, NH); 7.5–7.45 (*m*, 5 arom. H); 6.9–6.85 (*m*, 4 arom. H); 3.72 (*s*, MeO); 2.51 (*d*, J = 5.0, MeN). ^{13}C-NMR: 159.0 (*s*, C(3)); 156.8 (*s*, 1 arom. C); 154.2 (*s*, C(5)); 146.6, 140.9 (2*s*, 2 arom. C); 130.5, 129.5, 127.0, 120.9, 115.2 (5*d*, 9 arom. CH); 113.4 (*s*, C(4)); 55.6 (*q*, MeO); 32.3 (*q*, MeN). ESI-MS: 379 ($[M + Na]^+$), 357 ($[M + H]^+$). Anal. calc. for $C_{17}H_{16}N_4O_3S$ (356.40): C 57.29, H 4.52, N 15.72, S 9.00; found: C 56.93, H 4.40, N 15.95, S 8.88.

*2-Methyl-4-nitro-*N*-phenyl-3-(phenylamino)isothiazol-5(2*H*)-imine* (**12h**): Chromatography (hexane/AcOEt/CH_2Cl_2): 0.5 g (46%). Yellow crystals. M.p. 168–170°. IR: 3440 (br.), 3160 (br.), 3065 (sh), 3042*w*, 1635 (sh), 1615*s*, 1592*s*, 1570 (sh), 1545*s*, 1495*m*, 1487*m*, 1465*m*, 1455*m*, 1445*m*, 1435*m*, 1425 (sh), 1403*s*, 1370*s*, 1325*m*, 1300*s*, 1220*s*, 1190*s*, 1165*m*, 1152*s*, 1070*m*, 1025*w*, 985*w*, 958*w*, 993*w*, 975*m*, 895*w*, 883*w*, 840*w*, 825*w*, 772*m*, 760*m*, 750*m*, 740*w*, 690*s*. ^{1}H-NMR: 10.59 (*s*, NH); 7.45–7.3 (*m*, 6 arom. H); 7.23, 7.13 (2*t*, J = 7.3, 2 arom. H); 6.96 (*d*, J = 7.6, 2 arom. H); 2.89 (*s*, MeN). ^{13}C-NMR: 156.7 (*s*, C(3)); 154.4 (*s*, C(5)); 153.2, 138.2 (2*s*, 2 arom. C); 130.2, 129.7, 126.0, 125.0, 123.1, 119.8 (6*d*, 10 arom. CH); 114.3 (*s*, C(4)); 39.6 (*q*, MeN). ESI-MS: 349 ($[M + Na]^+$), 327 ($[M + H]^+$).

N*-(4-Methoxyphenyl)-2-methyl-4-nitro-3-(phenylamino)isothiazol-5(2*H*)-imine* (**12i**): Chromatography (hexane/AcOEt/CH_2Cl_2): 0.5 g (48%). Yellow crystals. M.p. 147–149°. IR: 3420 (br.), 3050*w*, 2830*w*, 1615*s*, 1585*s*, 1542*s*, 1503*s*, 1463*m*, 1455*m*, 1440 (sh), 1433*m*, 1403*s*, 1368*s*, 1300*s*, 1285*m*, 1240*s*, 1220*s*, 1180*s*, 1160*s*, 1100*m*, 1072*m*, 1032*s*, 983*m*, 940*m*, 928*m*, 910*m*, 888*m*, 825*m*, 800*w*, 765*m*, 750*m*, 725*m*, 698*m*. ^{1}H-NMR: 10.59 (br. *s*, NH); 7.4–7.1 (*m*, 5 arom. H); 7.1–6.8 (*m*, 4 arom. H); 3.74 (*s*, MeO); 2.90 (*s*, MeN). ^{13}C-NMR: 159.8 (*s*, 1 arom. C); 156.7 (*s*, C(3)); 154.6 (*s*, C(5)); 146.7, 136.7 (2*s*, 2 arom. C); 129.9, 127.2, 124.0, 121.0, 114.7 (5*d*, 9 arom. CH); 114.2 (*s*, C(4)); 56.0 (*q*, MeO); 39.5 (*q*, MeN). ESI-MS: 379 ($[M + Na]^+$), 357 ($[M + H]^+$).

*2-Benzyl-3-(benzylamino)-4-nitro-*N*-phenylisothiazol-5(2*H*)-imine* (**12j**): 1.1 g (85%). Yellow crystals. M.p. 175–176°. IR: 3220*w*, 3060*w*, 3020*w*, 1615*s*, 1600*s*, 1580*s*, 1505 (sh), 1500*s*, 1480*s*, 1455*s*, 1445 (sh), 1425*s*, 1380*s*, 1350*s*, 1320*m*, 1295*m*, 1268*s*, 1230*m*, 1210*m*, 1190*w*, 1175*w*, 1165 (sh), 1155*w*, 1135*s*, 1080*m*, 1070*m*, 1045*m*, 1025*m*, 1015 (sh), 1000*w*, 980*w*, 970*w*, 945*m*, 910*w*, 870*m*, 770*m*, 760*s*, 745*m*, 740*m*, 695*s*. ^{1}H-NMR: 9.92 (*t*, J = 5.6, NH); 7.4–7.2 (*m*, 12 arom. H); 7.07 (*t*, J = 7.4, 1 arom. H); 6.87 (*d*, J = 7.5, 2 arom. H); 4.92 (*s*, PhCH_2); 4.80 (*d*, J = 5.7, PhCH_2). ^{13}C-NMR: 159.7 (*s*, C(3)); 153.5 (*s*, C(5)); 152.7, 137.0, 134.5 (3*s*, 3 arom. C); 130.1, 129.2, 128.8, 128.3, 127.7, 127.5, 124.8, 119.7 (8*d*, 15 arom. CH); 113.3 (*s*, C(4)); 55.6, 49.0 (2*t*, PhCH_2). CI-MS: 418 (27), 417 (100, $[M + H]^+$).

*2-Methyl-3-(methylamino)-4-nitro-*N*-phenylisothiazol-5(2*H*)-imine* (**12k**): *Cf.* [20].

4. *2-(Benzothiazol-2-yl)-2-nitroethene-1,1-diamines* **13**: *General Procedure.* A soln. of **12** (0.07 mmol) in (D_6)DMSO (0.5 ml) was poured into a NMR tube. The isomerization was monitored by ^{1}H-NMR; the reaction times depended on the substituents of **12** (*cf. Fig. 3*). Then, the soln. was poured into ice water, and the precipitated solid was washed with H_2O and dried *in vacuo* overnight. The benzothiazolylethenediamines **13** were purified by prep. TLC[12]) (CH_2Cl_2/MeOH 100:1).

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[12]) In some cases, no purification was necessary. The precipitated **13** was only washed with MeOH and dried *in vacuo*.

2-(Benzothiazol-2-yl)-2-nitro-N,N'-*diphenylethene-1,1-diamine* (**13a**): 22 mg (83%). Yellow powder. M.p. 204–205°. IR: 3440 (br.), 3060*w*, 1610*m*, 1575 (sh), 1515*s*, 1530*s*, 1495 (sh), 1485*m*, 1455*m*, 1435*s*, 1370*m*, 1305*m*, 1230*m*, 1210*m*, 1175*w*, 1090*m*, 1075*w*, 1025*w*, 920*w*, 780*m*, 750*m*, 690*m*. ^{1}H-NMR (CD_2Cl_2): 14.04 (br. *s*, 2 NH); 7.92, 7.81 (2*dd*, J = 7.9, 1.3, 2 arom. H); 7.44, 7.35 (2*t*, J = 7.7, 2 arom. H); 7.1-6.9 (*m*, 10 arom. H). ^{13}C-NMR (CD_2Cl_2): 163.7 (*s*, C(1)); 154.1 (*s*, C(2')); 150.3, 136.7, 133.7 (3*s*, 4 arom. C); 129.1, 126.5, 126.3, 124.7, 124.1, 121.4, 121.0 (7*d*, 14 arom. CH); 114.1 (*s*, C(2)). EI-MS: 388 (10; $M^{+\cdot}$), 343 (23), 342 (100), 250 (13), 177 (28), 146 (13), 77 (14).

2-(Benzothiazol-2-yl)-N,N'-*bis(4-methoxyphenyl)-2-nitroethene-1,1-diamine* (**13b**): 30 mg (96%). Yellow powder. M.p. 180–182° (dec.). IR: 3010*w*, 2960*w*, 2930*w*, 2895*w*, 2830*w*, 2740 (br.), 1730*w*, 1715*w*, 1695*w*, 1685*w*, 1660*m*, 1650 (sh), 1645*s*, 1635*s*, 1615*s*, 1588*m*, 1565*s*, 1555*s*, 1540*s*, 1515*s*, 1505*s*, 1495 (sh), 1465 (sh), 1450*s*, 1440*s*, 1385*s*, 1340*s*, 1305*m*, 1290*s*, 1250*s*, 1235*s*, 1203*s*, 1180*s*, 1150*m*, 1130*w*, 1110*m*, 1078*s*, 1070*s*, 1012*m*, 980*m*, 940*w*, 925*w*, 890 (sh), 885 (sh), 872*m*, 862 (sh), 830*s*, 815 (sh), 805*m*, 780*w*, 765*s*, 750*m*, 730*m*. ^{1}H-NMR (CD_2Cl_2): 13.85 (br. *s*, 2 NH); 7.93, 7.80 (2*d*, J = 8.0, 2 arom. H); 7.44, 7.34 (2*t*, J = 7.7, 2 arom. H); 6.89, 6.60 (2*d*, J = 8.9, 8 arom. H); 3.68 (*s*, 2 MeO). ^{13}C-NMR (CD_2Cl_2): 163.9 (*s*, C(1')); 158.2 (*s*, 2 arom. C); 154.5 (*s*, C(2')); 150.4, 133.7, 129.5 (3*s*, 4 arom. C); 126.5, 125.9, 124.6, 121.3, 121.0, 114.3 (6*d*, 12 arom. CH); 114.0 (*s*, C(2)); 55.9 (*q*, 2 MeO). ESI-MS: 471 ($[M + Na]^+$), 449 ($[M + H]^+$).

2-(Benzothiazol-2-yl)-N,N'-*bis(4-fluorophenyl)-2-nitroethene-1,1-diamine* (**13c**): 26 mg (87%). Yellow crystals. M.p. 221–222°. IR: 3070*w*, 2920*w*, 2830*w*, 1660 (sh), 1645*s*, 1600*s*, 1572*s*, 1560*s*, 1515*s*, 1460 (sh), 1450*m*, 1435*m*, 1390*s*, 1345*s*, 1315*m*, 1298*m*, 1280*m*, 1235*s*, 1212*s*, 1158*s*, 1095*m*, 1080*s*, 1070*s*, 1015*w*, 980*m*, 960*m*, 975*w*, 875*m*, 865 (sh), 830*s*, 825*m*, 780*m*, 763*m*, 750*s*, 740 (sh), 720*m*, 705*m*, 695 (sh). ^{1}H-NMR (CD_2Cl_2): 14.02 (br. *s*, 2 NH); 7.93, 7.81 (2*ddd*, J = 8.0, 1.5, 0.8, 2 arom. H); 7.45, 7.36 (2*td*, J = 7.8, 1.4, 2 arom. H); 7.05–6.95 (*m*, 4 arom. H); 6.85–6.75 (*m*, 4 arom. H). ^{13}C-NMR (CD_2Cl_2): 163.7 (*s*, C(1)); 161.0 (*d*, ^1J(C,F) = 250.0, 2 arom. C); 155.1 (*s*, C(2')); 150.2, 133.7 (2*s*, 2 arom. C); 132.8 (*d*, ^4J(C,F) = 3.0, 2 arom. C); 126.6 (*d*, 1 arom. CH); 126.5 (*dd*, ^3J(C,F) = 8.6, 4 arom. CH); 124.8, 121.4, 121.0 (3*d*, 3 arom. CH); 116.0 (*dd*, ^2J(C,F) = 23.3, 4 arom. CH); 114.0 (*s*, C(2')). ESI-MS: 447 ($[M + Na]^+$), 425 ($[M + H]^+$).

2-(6-Methoxybenzothiazol-2-yl)-2-nitro-N,N'-*diphenylethene-1,1-diamine* (**13d**): 28 mg (95%). Yellow crystals. M.p. 192–194° (dec.). IR: 3050*w*, 3005*w*, 2920*w*, 2830*w*, 1730*w*, 1715*w*, 1695*w*, 1680*m*, 1670 (sh), 1660*s*, 1650 (sh), 1645*s*, 1635*s*, 1600*s*, 1580*s*, 1565*m*, 1540*s*, 1505*m*, 1495*m*, 1472*s*, 1449*s*, 1435*m*, 1413*s*, 1390*s*, 1345*s*, 1330*m*, 1315*m*, 1290*m*, 1282 (sh), 1260*m*, 1225*s*, 1200*s*, 1185*s*, 1175*s*, 1160*m*, 1122*m*, 1090*m*, 1070*s*, 1060*m*, 1025*m*, 995*w*, 975*m*, 915*m*, 910*m*, 885*w*, 830*m*, 815*w*, 782*w*, 765*m*, 752*s*, 698*m*. ^{1}H-NMR (CD_2Cl_2): 14.02 (br. *s*, 2 NH); 7.70 (*d*, J = 8.9, 1 arom. H); 7.36 (*d*, J = 2.5, 1 arom. H); 7.1–6.9 (*m*, 11 arom. H); 3.86 (*s*, MeO). ^{13}C-NMR (CD_2Cl_2): 161.5 (*s*, C(1)); 157.7 (*s*, 1 arom. C); 154.0 (*s*, C(2')); 144.8, 136.7, 135.2 (3*s*, 4 arom. C); 129.1, 126.3, 124.1, 121.7, 116.2 (5*d*, 12 arom. CH); 114.0 (*s*, C(2)); 103.4 (*d*, 1 arom. CH); 56.2 (*q*, MeO). ESI-MS: 441 ($[M + Na]^+$), 419 ($[M + H]^+$).

2-Nitro-(6-nitrobenzothiazol-2-yl)-N,N'-*diphenylethene-1,1-diamine* (**13e**): 18 mg (61%). Yellow crystals. M.p. 239–240° (dec.). IR: 3441*m*, 3097*m*, 3080*m*, 3062*m*, 2930*m*, 2860*m*, 2758*m*, 1651*s*, 1596*s*, 1585 (sh), 1565 (sh), 1552*s*, 1515 (sh), 1509*s*, 1503*s*, 1450*s*, 1436*s*, 1396*s*, 1348 (sh), 1338*s*, 1323*s*, 1300*s*, 1290*s*, 1230*s*, 1216*s*, 1178*m*, 1158*w*, 1132*m*, 1086*s*, 1074*s*, 1051*m*, 1028*w*, 1004*w*, 981*w*, 903*m*, 883*w*, 870*w*, 851*w*, 828*m*, 788*w*, 772*m*, 753*s*, 720*m*, 692*s*, 648*w*, 622*m*. ^{1}H-NMR (CD_2Cl_2): 13.74 (br. *s*, 2 NH); 8.83 (*d*, J = 2.3, 1 arom. H); 8.30 (*dd*, J = 9.0, 2.3, 1 arom. H); 7.86 (*d*, J = 9.0, 1 arom. H); 7.0–6.85 (*m*, 10 arom. H). ^{13}C-NMR (CD_2Cl_2): 168.8 (*s*, C(1)); 154.3 (*s*, C(2')); 153.9 (*s*, 1 arom. C); 144.5, 136.3, 134.0 (3*s*, 4 arom. C); 129.2, 126.8, 124.4, 121.0, 118.2 (6*d*, 13 arom. CH); 114.8 (*s*, C(2)). ESI-MS: 456 ($[M + Na]^+$), 434 ($[M + H]^+$).

(E)-2-(Benzothiazol-2-yl)-N-*methyl-2-nitro*-N'-*phenylethene-1,1-diamine* (**13f**). 18 mg (81%). Yellow crystals. M.p. 184–185°. IR: 3050*w*, 2980*w*, 2930*w*, 2680 (br.), 1695*w*, 1660 (sh), 1650 (sh), 1645*s*, 1635 (sh), 1608*s*, 1590*s*, 1575*s*, 1560 (sh), 1555 (sh), 1540*m*, 1505*m*, 1495*s*, 1490*s*, 1470*m*, 1455 (sh), 1450*s*, 1435*s*, 1420*s*, 1400*s*, 1380*s*, 1360 (sh), 1350 (sh), 1318*m*, 1290*s*, 1275 (sh), 1250*w*, 1240*s*, 1230*s*, 1200*m*, 1160*w*, 1128*w*, 1105*s*, 1080*m*, 1038*s*, 1025*w*, 1012*w*, 995*w*, 930 (sh), 920*m*, 865 (sh), 860*w*, 840*w*, 803*m*, 793*m*, 770*w*, 760*m*, 750*s*, 725*m*, 695*m*, 680*s*. ^{1}H-NMR (CD_2Cl_2): 13.72, 12.18 (2 br. *s*, 2 NH); 7.91, 7.79 (2*d*, J = 7.7, 2 arom. H); 7.5–7.25 (*m*, 7 arom. H); 2.73 (*d*, J = 5.3, MeN). ^{13}C-NMR (CD_2Cl_2): 163.9 (*s*, C(1)); 157.9 (*s*, C(2')); 150.5, 138.1, 133.7 (3*s*, 3 arom. C); 129.8, 127.0, 126.4, 125.1, 124.5, 121.3, 120.9 (7*d*, 9 arom. CH); 113.8 (*s*, C(2)); 33.4 (*q*, MeN). ESI-MS: 349 ($[M + Na]^+$), 327 ($[M + H]^+$).

(E)-2-(6-Methoxybenzothiazol-2-yl)-N-*methyl-2-nitro*-N'-*phenylethene-1,1-diamine* (**13g**): 23 mg (92%). Yellow crystals. M.p. 168–169° IR: 3280*w*, 3140*w*, 3150*w*, 3000*w*, 2960*w*, 2930*w*, 1655 (sh), 1650*s*, 1603*s*, 1568 (sh), 1555*s*, 1505 (sh), 1495*s*, 1470*s*, 1460*s*, 1455*s*, 1435*s*, 1415*s*, 1385*s*, 1340*s*, 1315*s*, 1280*s*, 1262*s*, 1220*s*, 1205 (sh), 1170*m*, 1145*s*, 1113*s*, 1070*m*, 1060 (sh), 1025*s*, 1015 (sh), 985*m*, 955*m*, 940*m*, 922*m*, 895*m*, 875*m*, 862*m*, 833*m*, 815*m*, 800*m*, 780*m*, 765*m*, 750 (sh), 745*m*, 695*s*. ^{1}H-NMR: 10.85, 10.32 (2 br. *s*, 2 NH); 7.58 (*d*, J = 8.8, 1 arom. H);

7.5–6.9 (*m*, 7 arom. H); 3.77 (*s*, MeO); 3.14 (br. *s*, MeN). ^{13}C-NMR: 159.5 (*s*, C(1)); 158.9 (*s*, C(2')); 155.4, 147.1, 136.8, 134.1 (4*s*, 4 arom. C); 129.4, 126.8, 123.7, 120.6, 114.4 (5*d*, 7 arom. CH); 109.5 (*s*, C(2)); 103.9 (*d*, 1 arom. CH); 55.5 (*q*, MeO); 30.2 (*q*, MeN). ESI-MS: 379 ([*M* + Na]$^+$), 357 ([*M* + H]$^+$).

(Z)-2-(Benzothiazol-2-yl)-N-*methyl-2-nitro*-N'-*phenylethene-1,1-diamine* (**13h**): 19 mg (82%). Pale yellow crystals. M.p. 182–183°. IR: 3045*w*, 2670 (br.), 1658 (sh), 1650*s*, 1605*s*, 1590*s*, 1575*s*, 1505 (sh), 1490*s*, 1450*s*, 1435*s*, 1420*s*, 1400*s*, 1380*s*, 1360*s*, 1350*s*, 1320*m*, 1290*s*, 1275 (sh), 1260*m*, 1240*s*, 1230*s*, 1200*m*, 1158*m*, 1105*s*, 1080*m*, 1035*s*, 1025*m*, 1013*w*, 995*w*, 930 (sh), 920*m*, 860*m*, 840*w*, 800*m*, 792*m*, 770*w*, 760*s*, 750*s*, 723*m*, 695*m*. ^{1}H-NMR: 10.85 (br. *s*, NH); 10.33 (br. *q*, NH); 7.9–7.15 (*m*, 9 arom. H); 3.16 (*d*, *J* = 5.0, MeN). ^{13}C-NMR: 161.4 (*s*, C(1)); 159.0 (*s*, C(2')); 152.7, 136.7, 132.7 (3*s*, 3 arom. C); 128.6, 126.8, 125.4, 123.7, 122.2, 120.9, 120.0 (7*d*, 9 arom. CH); 109.7 (*s*, C(2)); 30.2 (*q*, MeN). ESI-MS: 349 ([*M* + Na]$^+$), 327 ([*M* + H]$^+$).

(Z)-2-(6-Methoxybenzothiazol-2-yl)-N-*methyl-2-nitro*-N'-*phenylethene-1,1-diamine* (**13i**): 22 mg (90%). Yellow crystals. M.p. 170–172°. IR: 3440 (br.), 3060*w*, 3000*w*, 2960*w*, 2930*w*, 2830*w*, 2720*w*, 1660 (sh), 1645*s*, 1605*s*, 1585 (sh), 1570 (sh), 1555*s*, 1505*m*, 1470*s*, 1453*s*, 1435*s*, 1420*m*, 1382*s*, 1340*s*, 1320*s*, 1288*s*, 1265*s*, 1220*s*, 1205*s*, 1170*m*, 1145*s*, 1020*m*, 1030*m*, 985*m*, 955*m*, 920*w*, 863*m*, 840*m*, 825*m*, 813*m*, 800*m*, 780*m*, 765*m*, 743*m*, 705*m*, 693*m*. ^{1}H-NMR: 10.83 (br. *s*, NH); 10.32 (br. *q*, NH); 7.65–6.9 (*m*, 8 arom. H); 3.77 (*s*, MeO); 3.13 (*d*, *J* = 5.0, MeN). ^{13}C-NMR: 159.4 (*s*, C(1)); 158.9 (*s*, C(2')); 155.3, 147.0, 136.7, 134.0 (4*s*, 4 arom. C); 128.5, 126.7, 123.7, 120.6, 114.3 (5*d*, 7 arom. Ch); 109.4 (*s*, C(2)); 103.8 (*d*, 1 arom. CH); 55.5 (*q*, MeO); 30.1 (*q*, MeN). ESI-MS: 379 ([*M* + Na]$^+$), 357 ([*M* + H]$^+$).

2-(Benzothiazol-2-yl)-N,N'-*dibenzyl-2-nitroethene-1,1-diamine* (**13j**): 24 mg (81%). Yellow crystals. M.p. 192–193°. IR: 3150*m*, 3060*m*, 3020*m*, 2950*m*, 2920*m*, 2860*m*, 1725*w*, 1660 (sh), 1640*s*, 1605*s*, 1595*m*, 1560*m*, 1498*m*, 1475*s*, 1455*s*, 1435*s*, 1375*s*, 1365*s*, 1345*m*, 1288*s*, 1270*s*, 1255*m*, 1245*s*, 1220*s*, 1188*m*, 1155*m*, 1140*s*, 1130*s*, 1085*s*, 1075*s*, 1042*s*, 1030*m*, 1025 (sh), 1003*w*, 990*w*, 980*m*, 965*w*, 955*m*, 930*w*, 910*m*, 850*w*, 825*w*, 805*w*, 760*s*, 755 (sh), 735*s*, 725*s*. ^{1}H-NMR: 10.35, 9.63 (2 br. *s*, 2 NH); 7.92 (*d*, *J* = 7.5, 1 arom. H); 7.85–7.1 (*m*, 13 arom. H); 4.74, 4.39 (2 br. *s*, 2 PhCH_2). ^{13}C-NMR: 161.4 (*s*, C(1)); 159.4 (*s*, C(2')); 152.8, 136.3, 135.4, 132.8 (4*s*, 4 arom. C); 128.3, 128.1, 127.7, 127.3, 127.1, 125.5, 122.3, 121.1, 119.9 (9*d*, 14 arom. CH); 108.6 (*s*, C(2)); 48.2, 45.0 (2*t*, 2 PhCH_2). ESI-MS: 439 ([*M* + Na]$^+$), 417 ([*M* + H]$^+$). Anal. calc. for $C_{23}H_{20}N_4O_2S$ (416.50): C 66.33, H 4.84, N 13.45, S 7.70; found: C 65.96, H 4.93, N 13.17, S 7.57.

2-(Benzothiazol-2-yl)-N,N'-*dimethyl-2-nitroethene-1,1-diamine* (**13k**): 11 mg (56%). Pale yellow crystals. M.p. 264–265° (dec.). IR: 3400*w*, 3170*m*, 3060*m*, 3020*m*, 2980*m*, 2965*m*, 2930*m*, 1695 (sh), 1660*s*, 1640 (sh), 1568*s*, 1540*w*, 1505*w*, 1465*s*, 1455 (sh), 1435*s*, 1420 (br.), 1405*s*, 1380*s*, 1340 (sh), 1323*s*, 1310 (sh), 1292*s*, 1250*s*, 1193*m*, 1165*w*, 1142*s*, 1128*s*, 1075*m*, 1042*m*, 1010*s*, 920*m*, 845*w*, 755*s*, 740*w*, 725*m*, 705*w*, 695*m*, 665*m*. ^{1}H-NMR (CD_2Cl_2): 9.64, 8.89 (2 br. *s*, 2 NH); 7.84, 7.67 (2*d*, *J* = 7.9, 2 arom. H); 7.34, 7.19 (2*t*, *J* = 7.9, 2 arom. H); 3.00, 2.91 (2 br. *s*, 2 MeN). ^{13}C-NMR (CD_2Cl_2): 161.7 (*s*, C(1)); 160.8 (*s*, C(2')); 153.4, 133.6 (2*s*, 2 arom. C); 125.6, 122.6, 121.1, 120.4 (4*d*, 4 arom. CH); 109.3 (*s*, C(2)); 30.5, 29.5 (2 br. *q*, MeN). ESI-MS: 287 ([*M* + Na]$^+$).

5. *α-[(Benzothiazol-2-yl)nitromethylidene]*-N-*methylpyrrolidine-1-methanamine* (**13l**). *Cf.* [20]: 4.1 g (41%). Brown yellow powder. M.p. 300–303° (dec.). IR: 3441*m*, 3181*m*, 3058*m*, 2985*m*, 2945*m*, 2880*m*, 1644*s*, 1593*m*, 1522*m*, 1468*s*, 1437*s*, 1405 (sh), 1360 (sh), 1349*s*, 1333*m*, 1285*s*, 1250*m*, 1200*w*, 1185*w*, 1133*s*, 1123 (sh), 1105*m*, 1075*w*, 1029*m*, 978*w*, 952*m*, 877*w*, 853*w*, 826*w*, 759*m*, 726*w*. ^{1}H-NMR: 8.81 (br. *s*, NH); 7.93, 7.67 (2 br. *d*, 2 arom. H); 7.35, 7.21 (2 br. *s*, 2 arom. H); 3.57, 3.34 (2 br. *s*, 2 CH_2N); 2.80 (*s*, MeN); 2.07, 1.86 (2 br. *s*, 2 CH_2). ^{13}C-NMR: 160.1 (*s*, C(1)); 157.7 (*s*, C(2')); 152.9, 132.8 (2 *s*, 2 arom. C); 125.5, 122.4, 121.1, 120.1 (4*d*, 4 arom. CH); 108.1 (*s*, C(2)); 49.7, 47.9 (2*t*, 2 CH_2N); 30.5 (*q*, MeN); 24.6, 24.3 (2*t*, 2 CH_2). ESI-MS: 327 ([*M* + Na]$^+$), 305 ([*M* + H]$^+$).

6. *Crystal Structure Determination of* **11k**, **11l**, **12e**, *and* **13a** (see *Table 5* and *Figs. 1, 2,* and *4*)[13]). The intensities were collected on a *Rigaku-AFC5R* diffractometer using graphite-monochromated radiation from a 12-kW rotating-anode generator. The intensities were corrected for *Lorentz* and polarization effects, and a semiempirical absorption correction, based on ψ-scans, was applied for **13a** [43]. Data collection and refinement parameters are listed in *Table 5*, views of the molecules are shown in *Figs. 1, 2,* and *4*. The structures were solved by direct methods using SHELXS86 [44], which revealed the positions of all non-H-atoms. In **11l**, the 5-membered ring is disordered with two distinct conformations having the relative populations 0.866: 0.134. Resolution of the disorder was achieved by defining two positions for C(11) and C(12). The non-H-atoms were refined anisotrop-

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[13]) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-10/33. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44(0)1223 33 60 33; or email: teched@chemcrys.cam.ac.uk).

ically, except for those of the minor disordered conformation of **11l**, which were only refined isotropically. All of the H-atoms of **11k**, **11l**, and **12e**, as well as those of the NH groups of **13a**, were located in difference electron density maps, and their positions were allowed to refine. The H-atoms bonded to the C-atoms of the minor conformation of **11l** were not included in the model. The H-atoms bonded to the C-atoms of **13a** were fixed in geometrically calculated positions with a C–H distance of 0.95 Å. Individual isotropic displacement parameters were refined for all H-atoms in each structure. All refinements were carried out on F using full-matrix least-squares procedures. A correction for secondary extinction was applied in the case of **13a**. Neutral-atom scattering factors for non-H-atoms were taken from [45a] and the scattering factors for H-atoms form [46]. Anomalous dispersion effects were included in F_{calc} [47]; the values of f' and f'' were those of [45b]. All calculations were performed using the TEXSAN crystallographic software package [48].

Table 5. *Crystallographic Data for Compounds* **11k**, **11l**, **12e**, *and* **13a**

	11k	**11l**	**12e**	**13a**
Crystallized from	EtOH	acetone	CH_2Cl_2/hexane	EtOH
Empirical formula	$C_{11}H_{14}N_4O_2S$	$C_{14}H_{18}N_4O_2S$	$C_{21}H_{15}N_5O_4S$	$C_{21}H_{16}N_4O_2S$
Formula weight	266.32	306.38	433.44	388.44
Crystal color, habit	yellow, prism	yellow, prism	yellow, prism	yellow, needle
Crystal temp. [K]	173(1)	173(1)	173(1)	297(1)
Radiation, wavelength [Å]	MoK_α, 0.71069	MoK_α, 0.71069	MoK_α, 0.71069	CuK_α, 1.54178
Crystal dimensions [mm]	0.18 × 0.33 × 0.37	0.25 × 0.45 × 0.50	0.23 × 0.30 × 0.40	0.06 × 0.20 × 0.43
Crystal system	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	*Pbca*
Z	4	4	4	8
Reflections for cell determination	25	25	25	25
2θ range for cell determination [°]	$39 < 2\theta < 40$	$37 < 2\theta < 40$	$34 < 2\theta < 40$	$81 < 2\theta < 93$
Unit cell parameters a [Å]	13.664(3)	12.403(3)	12.168(6)	6.8924(9)
b [Å]	11.903(3)	11.528(5)	6.288(7)	23.974(2)
c [Å]	8.118(4)	10.988(5)	25.730(4)	22.4714(6)
β [°]	103.00(2)	95.05(2)	97.23(2)	90
V [Å^3]	1286.5(7)	1564.9(8)	1953(2)	3713.1(6)
D_{calc} [g cm^{-3}]	1.375	1.300	1.474	1.390
Absorption coefficient μ [mm^{-1}]	0.252	0.217	0.207	1.760
Transmission factors (min, max)	–	–	–	0.784; 1.000
Scan type	$\omega/2\theta$	$\omega/2\theta$	ω	$\omega/2\theta$
2θ (max) [°]	60	55	55	120
Total reflections measured	4180	3960	5118	3941
Symmetry-independent reflections	3760	3592	4485	2757
Reflections observed ($I > 2\sigma(I)$)	3014	2754	2788	1928
Variables	219	271	340	276
Final R	0.0396	0.0489	0.0452	0.0423
R_w[a])	0.0396	0.0525	0.0395	0.0433
Weights: p in $1/w = \sigma^2(F_o) + (pF_o)^2$	0.005	0.005	0.005	0.0075
Goodness of fit s	1.944	2.288	1.458	1.713
Final Δ_{max}/σ	0.0003	0.0004	0.0003	0.0002
$\Delta\rho$(max, min) [e Å^{-3}]	0.45, −0.23	0.33, −0.30	0.36, −0.26	0.16, −0.23

[a]) Function minimized $\sum w(|F_o| - |F_c|)^2$.

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