202. 3-(Acylamino)-3-amino-2-nitroacrylonitriles from *N*-Acyl-*S*-methyl-3,3-diamino-2-nitroacrylthioimidates

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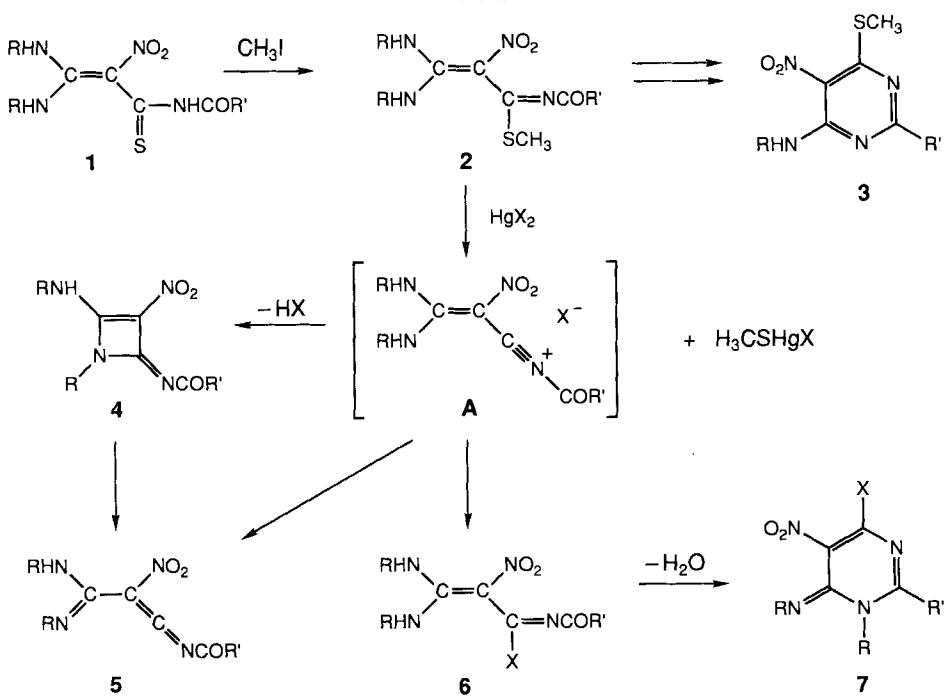
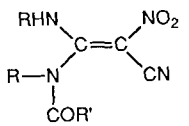
Reaction of *N*-acyl-3,3-diamino-2-nitroacrylthioamides **1** with MeI at room temperature leads to *N*-acyl-*S*-methyl-3,3-diamino-2-nitroacrylthioimidates **2** in moderate yields. The latter react with $Hg(OAc)_2$ in DMF yielding 3-(acylamino)-3-amino-2-nitroacrylonitriles **8**. The structures of **2a** and **8a** were established by X-ray crystallography.

1. Introduction. – Reactions of organic sulfur compounds induced by metal ions are well documented [1]. Thus, thioethers are obtained from thiols [2] and acid anhydrides from thiono esters [3] under mild conditions, thioketals are hydrolyzed to ketones [4] [5], thiolo- or thiono-esters to esters [6] [7], disulfides to sulfinic acids and thiols [8], thioethers to alcohols [9], thiocarbamates to carbamates [10], and 1-amino-1-(methylthio)-2-nitroethylenes to nitroacetamides [11]. We have already shown that 3,3-diamino-2-nitroacrylthioamides **1** are starting materials for the synthesis of pyrimidine derivatives **3**

Scheme 1



via the intermediate *N*-acyl-*S*-methyl-3,3-diamino-2-nitroacrylthioimidates **2** [12] [13]. With the aim to synthesize new heterocyclic compounds, we investigated the behavior of **2** towards mercury salts. Desulfurization of **2** by means of mercury salts could lead to two different heterocyclic systems depending on the mode of stabilization of nitrilium ion **A**. By intramolecular nucleophilic attack of one amino group, 3-nitroazetines **4** could be formed. Electrocyclic ring opening would then lead to ketene imines **5**, which also could be formed directly from **A**. On the other hand, the ion pair **A** could collapse to give **6** and, *via* cyclization and dehydration, 5-nitropyrimidines of type **7** (*Scheme 1*).



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However, instead of the expected heterocycles, 3-(acylamino)-3-amino-2-nitroacrylonitriles **8** were obtained on treatment of **2** with $Hg(OAc)_2$ in DMF.

2. Results and Discussion. – The *N*-acyl-3,3-diamino-*S*-methyl-2-nitroacrylthioimidates **2a–f** were obtained by methylation of the corresponding acrylthioamide derivatives **1** with MeI in DMF at room temperature in the presence of Ag_2O to trap the liberated HI. Attempts to neutralize HI with K_2CO_3 proved to be disadvantageous. In the presence of base, the formation of *N*,*S*-dimethylated products was favored. The alkylation was carried out at room temperature to avoid the formation of cyclization products, *e.g.* 4-(methylthio)pyrimidine derivatives **3** [12] [13].

The *N*-acyl-3,3-diamino-*S*-methyl-2-nitroacrylthioimidates **2** were purified by flash column chromatography or by recrystallization from EtOH (*Tab. 1*).

Table 1. *Synthesized* 'N-*acyl*-S-*methyl-3,3-diamino-2-nitroacrylthioimidates*' **2**

Compound	R	R′	Yield [%]	Compound	R	R′	Yield [%]
2a	CH_3	Ph	64	**2d**	$PhCH_2CH_2$	Fu	63
2b	CH_3	Fu[a])	71	**2e**	$PhCH_2$	Ph	71
2c	$PhCH_2CH_2$	Ph	77	**2f**	$PhCH_2$	Fu	73

[a]) Fu = 2-furyl.

Broad signals from the H- and C-atoms in the ^{1}H- and ^{13}C-NMR spectra, respectively, of **2** in (D_6)DMSO at room temperature hint to a slow interconversion of two conformers (around the C–N(amino) bonds) [14]. This assumption was confirmed by the bond lengths in the crystal structure of the methyl thioimidate **2a** (*cf. Fig. 1*; see *Sect. 3*).

Under the conditions of the methylation, *N*,*S*-dimethylated derivatives are formed as side-products in 4–10% yield. In the case of **2b**, the methylation was also carried out in the presence of K_2CO_3, and the yield of the *N*,*S*-dimethylated derivative **9b** reached 15%. Furthermore, the hydrolysis products of **2**, the 3,3-diamino-2-nitroacrylamides **10**, were

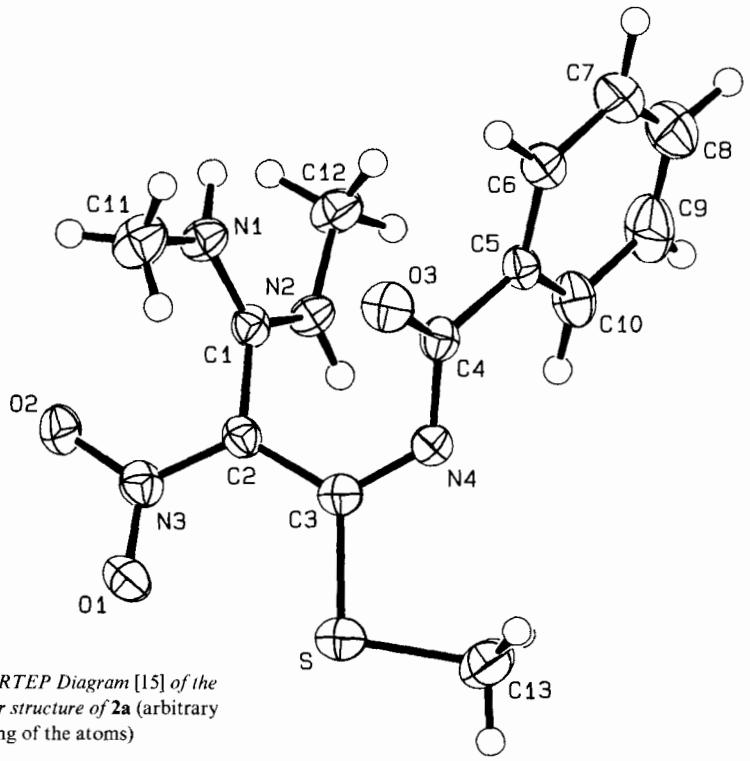
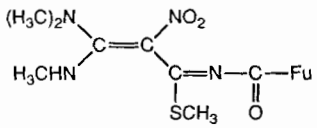
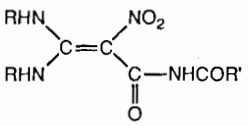


Fig. 1. *ORTEP Diagram* [15] *of the molecular structure of* **2a** (arbitrary numbering of the atoms)



9b



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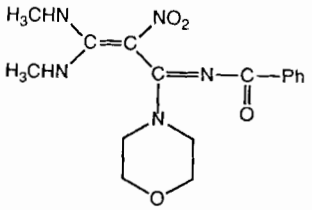

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detected in the reaction mixture (TLC). Treatment of **2a** with morpholine in refluxing acetone leads to the amidine **11** in 90% yield.

The desulfurization of **2** was carried out with $Hg(OAc)_2$ in DMF at room temperature. Two major products were obtained in this reaction, the nitriles **8** (*Tab. 2*) and the amides **10**, which again were separated by flash column chromatography using CH_2Cl_2 and CH_2Cl_2/MeOH mixtures[1]). The nitriles **8** were obtained as colorless crystals that slowly darken.

The CI-MS of **8** (NH_3 as ionization gas) show small $[M + 1]^+$ peaks, and $[M + 17 + 1]^+$ peaks, which are generally the base peaks. In the ^{1}H-NMR spectra, only one NH signal appears besides the absorptions of R and R′, and an intensive IR

[1]) A similar behavior of thioimidate esters toward Hg salts has been reported by *Hall* and *Satchell* [16].

Table 2. *Synthesized '3-(Acylamino)-3-amino-2-nitroacrylonitriles'* **8**

Compound	R	R′	Yield [%]	Compound	R	R′	Yield [%]
8a	CH_3	Ph	85	**8d**	$PhCH_2CH_2$	Fu[a])	71
8b	CH_3	Fu	57	**8e**	$PhCH_2$	Ph	58
8c	$PhCH_2CH_2$	Ph	46	**8f**	$PhCH_2$	Fu	74

[a]) Fu = 2-furyl.

absorption at 2210 cm^{-1} is characteristic for the CN group. In the ^{13}C-NMR spectra, the signal of the nitrile C-atom appears in the characteristic region of 101–104 ppm. Surprisingly, in the benzoyl derivatives signal duplication corresponding to two conformers can be observed. The structure of **8a** was confirmed by X-ray analysis (*Fig. 2*), structures of the other derivatives were elucidated by comparison of their spectroscopic data with those of **8a**.

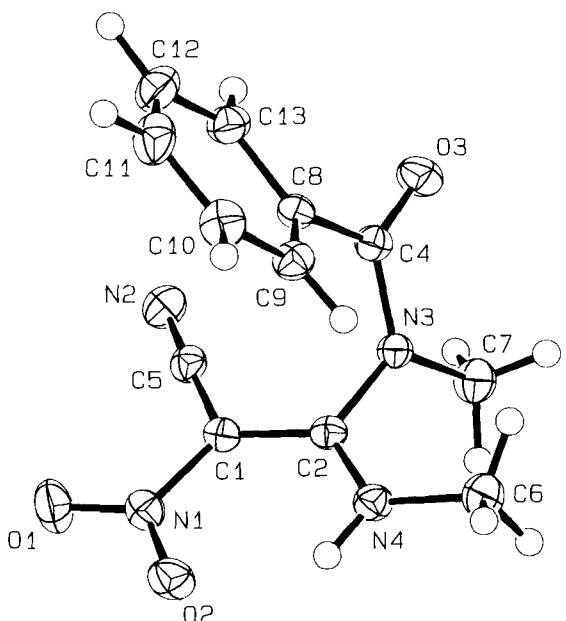
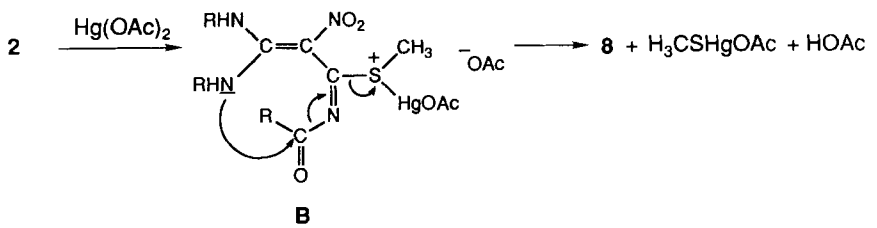


Fig. 2. *ORTEP Diagram* [15] *of the molecular structure of* **8a** (arbitrary numbering of the atoms)

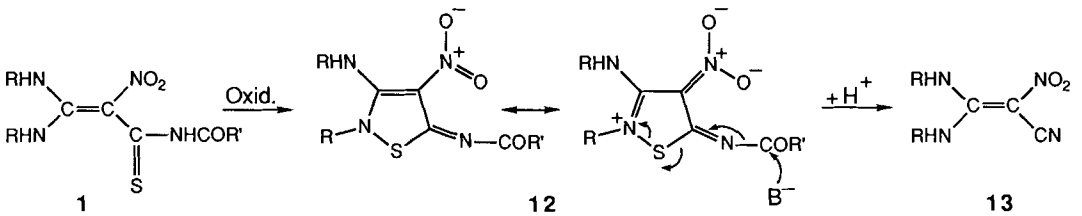
A reaction mechanism *via* an intramolecular acylation reaction explains the formation of **8** from **2** (*Scheme 2*). The attack onto the acyl group by the amino group *trans* to the NO_2 group is facilitated by coordination of the MeS group with Hg^{2+} and the subsequent cleavage of MeSHgOAc.

The formation of nitriles **8** from thioamides **1** has some precedent. For example, *Rajappa et al.* reported the synthesis of 3,3-diamino-2-nitroacrylonitriles **13** by base-induced fragmentation of the 4-nitroisothiazolines **12**, which are prepared by oxidation of **1** with Br_2 in AcOH [17] (*Scheme 3*).

Scheme 2



Scheme 3



Several other syntheses of nitriles starting from thioamides or thioimidates are described in the literature. Reagents such as P_2O_5 [18], dichlorocarbene [19], $CCl_4/Ph_3P/NEt_3$ [20], butyltin oxides [21], phosphorus tris(diethylamide) [22], elemental sulfur and $NaNO_2$ in liquid ammonia [23], formamide chlorides [24], diethylcarbamoyl chloride [25], phenylpropiolamidines [26], benzyl chloride under PTC conditions [27], bis(triphenylstannyl)carbodiimide [28], diphosphorous tetraiodide [29], DEAD/Ph_3P [30], and Hg salts [16] have been used for this purpose.

3. Crystal-Structure Determination of 2a and 8a. – Crystals of **2a** and **8a**, obtained from EtOH and acetone/MeOH, respectively, were used for X-ray structure determination. The intensities were collected on a *Rigaku AFC5R* rotating anode diffractometer using graphite-monochromated MoK_α radiation ($\lambda = 0.71069$ Å) and $\omega/2\theta$ scans. The intensities were corrected for *Lorentz* and polarization effects, and empirical absorption corrections were applied using DIFABS [31]. The structures were solved by direct methods using SHELXS86 [32], which revealed the positions of all non-H-atoms. All of the H-atoms were unambiguously located in difference-electron-density maps. Anisotropic refinement of the non-H-atoms and isotropic refinement of the H-atoms were carried out on F using full-matrix least-squares procedures [33], which minimized the function $\Sigma w(|F_o| - |F_c|)^2$. Corrections for secondary extinction were not applied. All calculations were performed with the TEXSAN crystallographic software package [34]. Data collection and refinement parameters are listed in *Tab. 3*[2]). Views of the molecules are shown in *Figs. 1* and *2*.

Since **2a** crystallized in a polar space group, an attempt was made to determine the absolute configuration of the structure. The atomic coordinates were refined together

[2]) Atomic coordinates, bond lengths, and bond angles have been deposited with the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 1EZ, England.

Table 3. *Crystallographic Data for Compounds* **2a** *and* **8a**

	2a	**8a**
Empirical formula	$C_{13}H_{16}N_4O_3S$	$C_{12}H_{12}N_4O_3$
Formula weight	308.35	260.25
Crystal color, habit	pale yellow, prism	colourless, prism
Crystal dimensions [mm]	0.20 × 0.22 × 0.41	0.20 × 0.28 × 0.42
Temp. [K]	173(1)	173(1)
Crystal system	orthorhombic	triclinic
Space group	$P2_12_12_1$	$P\bar{1}$
Reflections for cell determination	23	22
2θ range for cell determination [°]	34–38	39–40
a [Å]	10.090(6)	8.557(2)
b [Å]	16.140(9)	10.882(2)
c [Å]	9.363(4)	7.362(1)
α [°]	90	94.15(2)
β [°]	90	103.68(2)
γ [°]	90	107.39(2)
V [Å^3]	1525(1)	628.1(2)
Z	4	2
D_x [g cm^{-3}]	1.343	1.376
Absorption coefficient μ (MoK_α) [cm^{-1}]	2.170	0.960
Absorption correction (min; max)	0.689; 1.123	0.794; 1.079
$2\theta_{max}$ [°]	60	60
Reflection ranges (h; k; l)	0–14; −1–21; −1–13	0–12; −15–15; −10–10
Total reflections measured	2987	3882
Symmetry independent reflections	2875	3657
Reflections observed [$I > 3\sigma(I)$]	2081	2825
Variables	254	220
Final R	0.0365	0.0353
R_w	0.0294	0.0355
Weights w	$[\sigma^2(F_o) + (0.005F_o)^2]^{-1}$	$[\sigma^2(F_o) + (0.005F_o)^2]^{-1}$
Goodness of fit s	1.697	2.231
Final Δ_{max}/σ	0.0003	0.0002
$\Delta\rho$ (max; min) [e Å^{-3}]	0.20; −0.25	0.25; −0.18

with the enantiopole parameter [35] using the CRYSTALS program [36]. The enantiopole parameter refined to 0.1(1) (enantiomorphically pure crystals should yield either 0 or 1 for this parameter), which suggests that the refined atomic coordinates represent the true enantiomorph. The estimated standard deviation of this parameter is relatively high, because only a few *Friedel* pairs of reflections had been measured during the data collection.

An analysis of the bond lengths and torsion angles for **2a** (*Tables 4* and *5*) indicates that the formal bonding description of **2**, as shown in *Scheme 1*, is not strictly correct. The C(1)–C(2)[3]) bond length is only slightly shorter than a normal single bond, and the torsion angles about this bond indicate an average twist of *ca.* 63°. Therefore, this bond, which is formally described as a double bond, has all the properties of a single bond,

[3]) The arbitrary numbering of the atoms of *Figs. 1* and *2* is used in the discussion of the molecular structure of **2a** and **8a**.

Table 4. *Selected Bond Lengths* [Å] *for* **2a** (e.s.d.'s in parentheses)

S–C(3)	1.767(3)	O(3)–C(4)	1.237(3)	N(2)–C(12)	1.458(4)	C(1)–C(2)	1.482(4)
S–C(13)	1.806(4)	N(1)–C(1)	1.318(3)	N(3)–C(2)	1.354(3)	C(2)–C(3)	1.447(3)
O(1)–N(3)	1.258(3)	N(1)–C(11)	1.448(4)	N(4)–C(3)	1.295(3)	C(4)–C(5)	1.483(4)
O(2)–N(3)	1.281(3)	N(2)–C(1)	1.323(3)	N(4)–C(4)	1.375(3)		

Table 5. *Selected Torsion Angles* [°] *for* **2a**

S–C(3)–N(4)–C(4)	−156.9(2)	N(1)–C(1)–C(2)–N(3)	68.6(3)
S–C(3)–C(2)–N(3)	17.9(4)	N(1)–C(1)–C(2)–C(3)	−120.5(3)
S–C(3)–C(2)–C(1)	−152.4(2)	N(2)–C(1)–C(2)–N(3)	−113.8(3)
O(1)–N(3)–C(2)–C(1)	177.9(2)	N(2)–C(1)–C(2)–C(3)	57.0(3)
O(1)–N(3)–C(2)–C(3)	7.4(4)	N(3)–C(2)–C(3)–N(4)	−167.9(2)
O(2)–N(3)–C(2)–C(1)	−2.9(4)	N(4)–C(3)–C(2)–C(1)	21.9(4)
O(2)–N(3)–C(2)–C(3)	−173.4(2)	N(4)–C(4)–C(5)–C(6)	−170.8(2)
O(3)–C(4)–N(4)–C(3)	50.7(4)	N(4)–C(4)–C(5)–C(10)	10.1(4)
O(3)–C(4)–C(5)–C(6)	3.7(4)	C(2)–C(3)–N(4)–C(4)	28.7(4)
O(3)–C(4)–C(5)–C(10)	−175.5(3)	C(3)–N(4)–C(4)–C(5)	−134.9(3)

without any π-orbital overlap. The two C(1)–N(amine) bonds, which are substantially shorter than normal C–N bonds, but longer than normal C=N bonds, are equivalent. The C(2)–N(nitro) and the C(2)–C(3) bonds are of length usually found for delocalized π-bonds. Delocalization in this region is further supported by the near-planarity of the atoms C(1), C(2), C(3), and the NO_2 group. The N–O bond lengths in the NO_2 group are also slightly longer than the normally observed length of 1.22 Å. These observations can be explained by considering that the molecule exists in a zwitterionic form where the positive charge is delocalized between the amino groups and the negative charge is delocalized between the O-atoms of the NO_2 group. Such an affect can be described as the 'push-pull' nature of nitroenamines and has been discussed by *Rajappa* [14].

In the crystal lattice of **2a**, the molecules are bound by intermolecular H-bonds, as shown in *Fig. 3*. Each amine group of the molecule acts as a donor for intermolecular H-bonds. The corresponding acceptor atoms are the O-atom of the NO_2 group of a neighboring molecule, and the carbonyl O-atom of a different neighboring molecule. Independently, the two H-bonds links the molecules into infinite one-dimensional chains running parallel to the x-axis and the z-axis, respectively. The combination of both interactions links the molecules into a three-dimensional network.

Selected bond lengths and torsion angles for **8a** are given in *Tables 6* and *7*. The C(1)–C(2)[3]) bond is once again too long to be a formal double bond. The C(1)–C(2), C(1)–C(nitrile), C(1)–N(nitro), and C(2)–N(amide) bond lengths suggest that these atoms are linked by delocalized π-bonds. This is also supported by the observation that the region of the molecule involving C(1), C(2), N(3), N(4), the NO_2, and the CN groups is relatively planar. The C(1)–N(amine) bond is substantially shorter than a normal C–N bond. The bonding for **8a** can also be described as having the 'push-pull' zwitterionic form, where the positive charge is localized on the amine N-atom, and the negative charge is centred on the NO_2 group, which results in a delocalized π-bonding system extending from the NO_2 and CN groups across to the amide group.

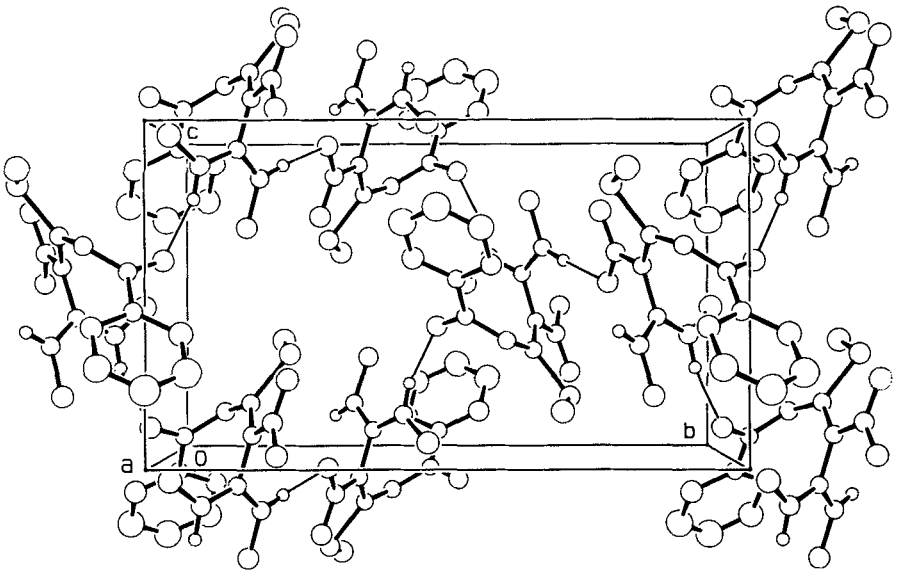


Fig. 3. *Molecular packing of* **2a** *projected down the* a-*axis showing the H-bonding scheme* (arbitrary spheres for atoms; uninvolved H-atoms omitted for clarity)

Table 6. *Selected Bond Lengths* [Å] *for* **8a** (e.s.d.'s in parentheses)

O(1)–N(1)	1.239(1)	N(2)–C(5)	1.151(1)	N(3)–C(7)	1.478(2)	C(1)–C(5)	1.421(2)
O(2)–N(1)	1.255(1)	N(3)–C(2)	1.409(1)	N(4)–C(2)	1.315(1)	C(4)–C(8)	1.493(2)
O(3)–C(4)	1.222(1)	N(3)–C(4)	1.388(1)	N(4)–C(6)	1.461(2)		
N(1)–C(1)	1.404(1)			C(1)–C(2)	1.402(2)		

Table 7. *Selected Torsion Angles* [°] *for* **8a**

O(1)–N(1)–C(1)–C(2)	−178.2(1)	N(3)–C(2)–C(1)–C(5)	6.5(2)
O(1)–N(1)–C(1)–C(5)	−3.6(2)	N(3)–C(4)–C(8)–C(9)	40.7(2)
O(2)–N(1)–C(1)–C(2)	1.1(2)	N(3)–C(4)–C(8)–C(13)	−143.8(1)
O(2)–N(1)–C(1)–C(5)	175.7(1)	N(4)–C(2)–N(3)–C(4)	−121.6(1)
O(3)–C(4)–N(3)–C(2)	−164.4(1)	N(4)–C(2)–N(3)–C(7)	73.1(1)
O(3)–C(4)–N(3)–C(7)	0.7(2)	N(4)–C(2)–C(1)–C(5)	−170.5(1)
O(3)–C(4)–C(8)–C(9)	−137.6(1)	C(1)–C(2)–N(3)–C(4)	61.2(1)
O(3)–C(4)–C(8)–C(13)	37.9(2)	C(1)–C(2)–N(3)–C(7)	−104.2(1)
N(1)–C(1)–C(2)–N(3)	−179.1(1)	C(2)–N(3)–C(4)–C(8)	17.2(2)
N(1)–C(1)–C(2)–N(4)	3.9(2)	C(7)–N(3)–C(4)–C(8)	−177.7(1)

In the crystal lattice of **8a**, the molecules are bound by weak intermolecular H-bonds, as shown in *Fig. 4*. The amino group is a H-bond donor to the CN N-atom of an adjacent molecule. This contact links the molecules into infinite one-dimensional chains which run parallel to the z-axis. The amine H-atom also forms a strong intramolecular H-bond with

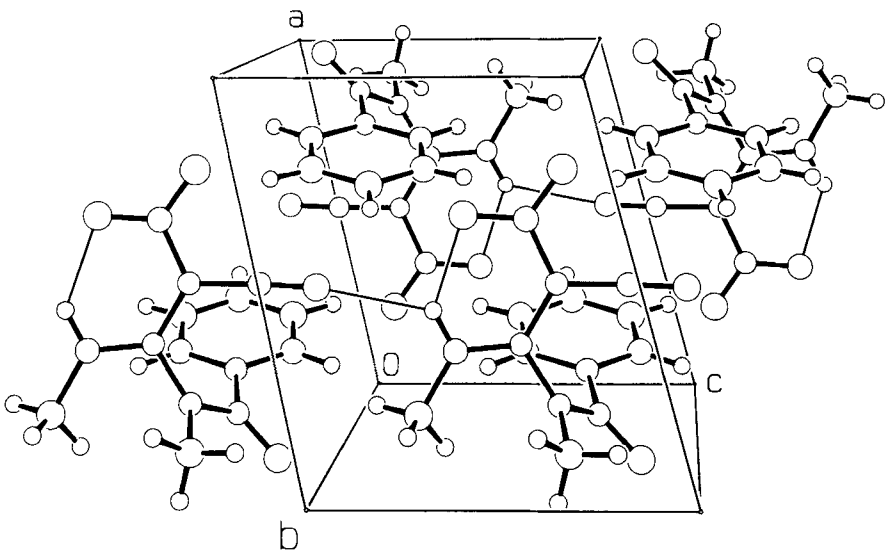


Fig. 4. *Molecular packing of* **8a** *projected down the* b-*axis showing the H-bonding scheme* (arbitrary spheres for atoms; uninvolved H-atoms omitted for clarity)

the adjacent O-atom of the NO_2 group, and can, therefore, be thought of as forming bifurcated H-bonds.

We thank Mr. *H. Frohofer* for elemental analyses and IR spectra, Mr. *T. Plüss*, Mr. *D. Rentsch*, and Mrs. *N. Walch* for NMR spectra, Mrs. Dr. *A. Lorenzi* for mass spectra and Mrs. *R. Pérez* for experimental collaboration. *M. I. G.* thanks the *Swiss Federal Government* for the provision of a *National Scholarship for Foreign Students.*

Experimental Part

1. *General.* TLC: silica gel *60* F_{254}-precoated plates (0.25 mm; *Merck*); $CHCl_3$/MeOH 10:1 and 20:1 as eluent mixtures. Column chromatography (flash chromatography): silica gel *60* (0.040–0.063 mesh; *Merck*). DMF was purchased from *Fluka* and dried with activated molecular sieves (4 Å). M.p.: *Mettler-FP-5* apparatus, uncorrected. IR spectra: in KBr on a *Perkin-Elmer-297* apparatus; absorption bands in cm^{-1}. ^{1}H-NMR spectra: at 300 MHz on a *Bruker AC-300* instrument in (D_6)DMSO (**2**) and (D_6)acetone (**8**), respectively. Chemical shifts in ppm relative to TMS (= 0 ppm); coupling constants *J* in Hz. ^{13}C-NMR spectra: in (D_6)DMSO on a *Varian XL-200* (50.4 MHz) instrument; chemical shifts in ppm relative to TMS (= 0 ppm). Signal multiplicity was indirectly interpreted from the DEPT spectra. MS: on a *Finnigan SSQ-700* instrument; CI-mode with NH_3 as ionization gas. Peaks (> 5%) are given in *m/z*. The starting acrylthioamides **1** were synthesized according to [12] [17] [37]. **1c**: M.p.: 169.6–169.7°; **1d**: M.p.: 170.6–171.1°.

2. *Synthesis of* N-*Acyl-3,3-diamino*-S-*methyl-2-nitroacrylthioimidates* **2**. *General Procedure.* To a cold soln. (5–10°) of 6.80 mmol of **1** in 13.6 ml of DMF, 3.40 mmol (788 mg) of Ag_2O and 13.6 mmol (0.85 ml) of MeI were added. The mixture was allowed to reach r.t. and was stirred for 2–3 h (TLC monitoring). The precipitated AgI was separated by centrifugation and washed with small portions of DMF. The DMF solns. were poured into an ice-water mixture, and the precipitated yellow solid was filtered, washed with H_2O and dried over P_2O_5 *in vacuo* overnight. The imidates were purified by column chromatography or by recrystallization from EtOH.

2.1. N-*[3,3-Bis(methylamino)-1-(methylthio)-2-nitroprop-2-enylidene]benzamide* (**2a**). Recrystallized from EtOH: 1.34 g (64%). Yellow crystals. M.p. 200.3–203.5°. IR: 3300*m*, 3190*m*, 3120*m*, 3075*m*, 3020*m*, 2970*m*, 2920*m*, 1650*s*, 1600*s*, 1570*s*, 1530*m*, 1490 (sh), 1450*m*, 1410*s*, 1385*m*, 1340 (sh), 1330*s*, 1310*s*, 1275*s*, 1250*s*, 1195*m*, 1170*m*, 1155 (sh), 1145*s*, 1120 (sh), 1080*w*, 1065*w*, 1050*w*, 1020*w*, 1005*m*, 950*m*, 940*m*, 895*s*, 855*m*, 800*s*, 775*s*, 760*s*, 715*s*, 685*s*, 670*m*, 650*s*, 620*s*. ^{1}H-NMR: 9.30, 8.61 (2 br., 2 NH); 7.88 (*d*, *J* = 7.7, 2 arom. H); 7.5–7.4 (*m*, 3 arom. H); 2.77, 2.40 (2 br. *s*, 2 *Me*NH); 2.21 (*s*, MeS). ^{13}C-NMR: 170.5 (*s*, C=O); 167.2 (*s*, C=N); 160.1 (*s*, MeNH)$_2$*C*=); 136.4 (*s*, 1 arom. C); 131.4, 128.8, 128.1 (3*d*, 5 arom. CH); 112.5 (*s*, =*C*(NO$_2$)C); 30.1, 28.1 (br., 2 MeNH); 14.7 (*q*, MeS). CI-MS: 310 (5), 309 (36, [*M* + 1]$^+$), 293 (11), 291 (6), 279 (20), 278 (100), 261 (18), 245 (23). Anal. calc. for $C_{13}H_{16}N_4O_3S$ (308.36): C 50.64, H 5.23, N 18.17, S 10.40; found: C 50.77, H 5.29, N 17.97, S 10.68.

2.2. N-*[3,3-Bis(methylamino)-1-(methylthio)-2-nitroprop-2-enylidene]furan-2-carboxamide* (**2b**). Synthesis according to the *General Procedure*, but in the presence of 6.8 mmol of anh. K_2CO_3 (without Ag_2O). The DMF soln. was poured into ice-water and extracted with CH_2Cl_2. The CH_2Cl_2 phase was washed once with sat. NaCl soln. and with H_2O, dried (Na_2SO_4), and the solv. removed *in vacuo*. The products were separated by column chromatography ($CHCl_3$/MeOH 20:1): **2b**: 1.44 g (71%). Yellow crystals. M.p. 190.4–190.8°. IR: 3220 (br.), 3100 (br.), 3060 (sh), 3000*m*, 2920*w*, 1645*s*, 1570 (sh), 1560*s*, 1550 (sh), 1490 (sh), 1470*s*, 1445 (sh), 1425 (sh), 1395*s*, 1355*s*, 1310*s*, 1290*s*, 1225*m*, 1210*m*, 1185*m*, 1170*m*, 1140*m*, 1115 (sh), 1080*s*, 1030*m*, 1010*m*, 980*s*, 920*s*, 880*m*, 840*w*, 780*m*, 755 (sh), 685*w*, 670 (sh), 610 (sh), 600*w*. ^{1}H-NMR: 9.31, 8.64 (2 br., 2 NH); 7.79 (br. *s*, H–C(5) of furan); 6.93 (*d*, *J*(3,4) = 3.2, H–C(3) of furan); 6.58 (*dd*, *J*(4,3) = 3.3, *J*(4,5) = 1.6, H–C(4) of furan); 2.76 (br., MeNH); 2.50 (MeNH, covered by DMSO signal); 2.19 (*s*, MeS). ^{13}C-NMR: 167.7 (*s*, C=N); 161.9 (*s*, C=O); 159.9 (*s*, (MeNH)$_2$*C*); 150.9 (*s*, C(2) of furan); 145.3 (*d*, C(5) of furan); 115.0 (*d*, C(3) of furan); 112.8 (*s*, =*C*(NO$_2$)C); 111.7 (*d*, C(4) of furan); 29.8, 29.5 (2 br., 2 MeNH); 14.7 (*q*, MeS). CI-MS: 300 (7), 299 (47, [*M* + 1]$^+$), 297 (7), 283 (11), 281 (9), 269 (16), 268 (100), 267 (14), 251 (9), 235 (7), 221 (7), 219 (10), 206 (7), 192 (10), 174 (8). Anal. calc. for $C_{11}H_{14}N_4O_4S$ (298.32): C 44.29, H 4.73, N 18.78, S 10.75; found: C 44.59, H 4.51, N 18.75, S 10.66.

N-*[3-(Dimethylamino)-3-(methylamino)-1-(methylthio)-2-nitroprop-2-enylidene]furan-2-carboxamide* (**9b**): 319 mg (15%). Yellow crystals. M.p. 90.0–91.3°. IR: 2970*m*, 2920*m*, 1640*s*, 1595 (sh), 1555*s*, 1545*s*, 1525*s*, 1510 (sh), 1495 (sh), 1465*s*, 1420*s*, 1385*s*, 1340 (sh), 1280 (br.), 1250 (br.), 1215*s*, 1205 (sh), 1160*s*, 1145 (sh), 1110*s*, 1075*m*, 1030*m*, 1005*s*, 960 (sh), 930*s*, 915*s*, 875*m*, 855*m*, 770*m*, 755*s*, 735*s*, 605*m*. ^{1}H-NMR ($CDCl_3$): 8.24 (br., NH); 7.44 (*d*, *J*(3,5) = 0.6, H–C(5) of furan), 6.91 (*d*, *J*(3,4) = 3.4, H–C(3) of furan); 6.41 (*dd*, *J*(4,3) = 3.4, *J*(4,5) = 1.7, H–C(4) of furan); 3.04, 2.92 (2*s*, 2 MeN); 2.88 (*d*, *J* = 3.3, MeNH); 2.28 (*s*, MeS). ^{13}C-NMR ($CDCl_3$): 169.2 (*s*, C=N); 162.8 (*s*, [Me$_2$N(MeNH)]*C*=); 161.0 (*s*, C=O); 150.6 (*s*, C(2) of furan); 145.1 (*d*, C(5) of furan); 115.6 (*d*, C(3) of furan); 111.7 (*d*, C(4) of furan); 41.1, 38.2 (2*q*, 2 MeN); 31.2 (*q*, MeN); 15.0 (*q*, MeS). CI-MS: 314 (10), 313 (65, [*M* + 1]$^+$), 297 (15), 285 (10), 283 (14), 282 (100), 281 (12), 269 (5), 268 (35), 265 (21). Anal. calc. for $C_{12}H_{16}N_4O_4S$ (312.35): C 46.14, H 5.16, N 17.94, S 10.26; found: C 46.24, H 5.38, N 17.70, S 10.36.

2.3. N-*[1-(Methylthio)-2-nitro-3,3-bis(2-phenylethylamino)prop-2-enylidene]benzamide* (**2c**). Recrystallized from EtOH: 2.56 g (77%). Yellow crystals. M.p. 71.0–72.1°. IR: 3210 (br.), 3060*m*, 3020*m*, 2970*m*, 2920*m*, 1640*s*, 1600*s*, 1565*s*, 1550*s*, 1495*m*, 1485*m*, 1450*m*, 1365*s*, 1325*s*, 1305*s*, 1280*s*, 1270*s*, 1240*s*, 1200*m*, 1170*s*, 1150*m*, 1095*w*, 1080*m*, 1060 (sh), 1050*w*, 1020*m*, 1000*w*, 960*w*, 930*m*, 920*m*, 810*w*, 790*m*, 750*m*, 700*m*, 645*m*, 620*w*. ^{1}H-NMR: 9.67, 8.79 (2 br., 2 NH); 7.96 (*d*, *J* = 7.2, 2 arom. H); 7.55–7.45 (*m*, 3 arom. H); 7.3–7.15 (*m*, 10 arom. H); 3.47, 3.42 (2*m*, 2 CH$_2$); 3.18, 2.80 (2 br., 2 CH$_2$); 2.21 (*s*, MeS). ^{13}C-NMR: 170.0 (*s*, C=O); 167.6 (*s*, C=N); 158.5 (*s*, (PhCH$_2$CH$_2$NH)$_2$*C*=); 138.2, 136.6 (2*s*, 3 arom. C); 128.8, 128.7, 128.5, 128.1, 126.4 (5*d*, 15 arom. CH); 112.8 (*s*, =*C*(NO$_2$)C); 40.4, 38.7 (2 br., 4 CH$_2$); 14.9 (*q*, MeS). CI-MS: 489 (< 1%, [*M* + 1]$^+$); 472 (9), 471 (25), 425 (12), 385 (8), 373 (12), 372 (10), 369 (8), 368 (40), 354 (10), 339 (7), 338 (15), 337 (12), 321 (7), 320 (6), 312 (14), 305 (5), 303 (5), 300 (6), 299 (37), 296 (6), 286 (16), 278 (22), 270 (5), 269 (32), 268 (6), 251 (7), 244 (6), 243 (27), 227 (7), 226 (42), 195 (12), 164 (9), 140 (19), 139 (100), 138 (14), 123 (7), 122 (86), 121 (10), 120 (8), 108 (16), 105 (39), 104 (28). Anal. calc. for $C_{27}H_{28}N_4O_3S$ (488.61): C 66.37, H 5.78, N 11.47, S 6.56; found: C 66.25, H 5.87, N 11.36, S 6.46.

2.4. N-*[1-(Methylthio)-2-nitro-3,3-bis(2-phenylethylamino)prop-2-enylidene]furan-2-carboxamide* (**2d**). Chromatography (CH_2Cl_2/MeOH 50:1): 2.05 g (63%). Yellow crystals. M.p. 81.5–83.5°. IR: 3210 (br.), 3120*m*, 3050*m*, 3020*m*, 2940*m*, 2920*m*, 1640*s*, 1600*s*, 1560 (sh), 1550*s*, 1530*s*, 1520 (sh), 1515 (sh), 1495*s*, 1470*s*, 1450*s*, 1430*s*, 1410*s*, 1395*s*, 1350*s* (br.), 1285*s* (br.), 1220*m*, 1195 (sh), 1170*s*, 1150*m*, 1100*m*, 1080*m*, 1030*w*, 1010*m*, 965*w*, 930 (sh), 920*m*, 880*m*, 830*w*, 790 (sh), 745*s*, 695*s*, 610*w*. ^{1}H-NMR: 9.67, 8.82 (2 br., 2 NH); 7.83 (br. *s*, H–C(5) of furan); 7.3–7.15 (*m*, 10 arom. H); 6.96 (*d*, *J*(3,4) = 3.2, H–C(3) of furan); 6.61 (*dd*, *J*(4,3) = 3.2, *J*(4,5) = 1.7, H–C(4) of furan); 3.3–3.25 (br., 2 CH$_2$); 2.8–2.6 (br., 2 CH$_2$); 2.20 (*s*, MeS). ^{13}C-NMR: 168.2 (*s*, C=N); 161.5 (*s*, C=O); 158.4 (*s*, (PhCH$_2$CH$_2$NH)$_2$*C*=); 151.3 (*s*, C(2) of furan); 145.2 (*d*, C(5) of furan); 138.2 (*s*, 2 arom. C); 128.6, 128.4, 126.4 (3*d*, 10 arom. CH); 114.9 (*d*, C(3) of furan); 113.3 (*s*, =*C*(NO$_2$)C); 111.8 (*d*, C(4) of furan); 45.2, 34.9 (2 br., 4 CH$_2$); 14.9 (*q*, MeS). CI-MS: 479 (5, [*M* + 1]$^+$), 463 (11), 462 (20), 461 (100), 450 (7), 449 (14), 448 (91). Anal. calc. for $C_{25}H_{26}N_4O_4$ (478.58): C 62.74, H 5.48, N 11.71, S 6.70; found: C 62.61, H 5.25, N 11.72, S 6.67.

2.5. N-*[3,3-Bis(benzylamino)-1-(methylthio)-2-nitroprop-2-enylidene]benzamide* (**2e**). Chromatography (CH_2Cl_2/MeOH 30:1): 2.21 g (71%). Yellow crystals. M.p. 91.2–93.6°. IR: 3200 (br.), 3050*m*, 3020*m*, 2960 (sh), 2920*m*, 1640*s*, 1595*s*, 1565*s*, 1550*s*, 1535*s*, 1525*s*, 1510*s*, 1495*s*, 1485 (sh), 1465 (sh), 1450*s*, 1430*s*, 1410*s*, 1375*s*, 1310*s*, 1285*s*, 1240*s*, 1165*s*, 1150*s*, 1105*m*, 1075*m*, 1060*m*, 1020*m*, 1000*w*, 965*w*, 940*m*, 920*m*, 880*m*, 815*m*, 795*m*, 775 (sh), 740*m*, 710 (sh), 695*s*, 655*m*, 615*w*. ^{1}H-NMR: 10.18, 9.43 (2 br., 2 NH); 7.89 (*d*, *J* = 7.2, 2 arom. H); 7.55–7.45 (*m*, 3 arom. H); 7.45–7.25 (*m*, 10 arom. H); 4.43, 4.45 (2*s*, 2 CH_2); 2.17 (*s*, MeS). ^{13}C-NMR: 169.6 (*s*, C=O); 169.0 (*s*, C=N); 159.5 (*s*, $(PhCH_2NH)_2C$=); 136.9 (*s*, 1 arom. C); 135.7 (br. *s*, 2 arom. C); 131.0, 128.8, 128.2, 127.9, 127.3 (5*d*, 7 arom. CH); 113.9 (*s*, $=C(NO_2)C$); 40.8–40.2 (br., 2 CH_2); 15.1 (*q*, MeS). CI-MS: 461 (43, $[M + 1]^+$), 430 (6), 409 (65), 379 (22), 354 (30), 326 (26), 309 (76), 284 (100), 275 (18), 255 (24), 221 (18), 212 (32), 196 (79), 181 (43). Anal. calc. for $C_{25}H_{24}N_4O_3S$ (460.56): C 65.20, H 5.25, N 12.16, S 6.96; found: C 65.17, H 5.40, N 12.09, S 7.26.

2.6. N-*[3,3-Bis(benzylamino)-1-(methylthio)-2-nitroprop-2-enylidene]furan-2-carboxamide* (**2f**). Chromatography (CH_2Cl_2/MeOH 300:1): 2.24 g (73%). Yellow crystals. M.p. 95.5–97.7°. IR: 3200 (br.), 3120*m*, 3050*m*, 3020*m*, 3000*m*, 2960 (sh), 2910*m*, 1640*s*, 1600 (sh), 1580 (sh), 1560 (sh), 1545*s*, 1535 (sh), 1525*s*, 1515 (sh), 1495*s*, 1475 (sh), 1470*s*, 1450*s*, 1430*s*, 1410*s*, 1390*s*, 1360*s*, 1340*s*, 1285 (br.), 1220*s*, 1170*s*, 1155 (sh), 1110*m*, 1075*m*, 1025*m*, 1005*m*, 965 (sh), 945 (sh), 920*m*, 880*m*, 825 (sh), 785*m*, 730*s*, 695*s*, 660 (sh), 610*w*. ^{1}H-NMR: 10.15, 9.42 (2 br., 2 NH); 7.83 (*d*, *J*(3,5) = 0.6, H–C(5) of furan); 7.30, 7.25 (2 br. *s*, 10 arom. H); 6.91 (*d*, *J*(3,4) = 3.3, H–C(3) of furan); 6.62 (*dd*, *J*(4,3) = 3.3, *J*(4,5) = 1.6, H–C(4) of furan); 4.44 (br., 2 CH_2); 2.18 (*s*, MeS). ^{13}C-NMR: 169.5 (*s*, C=N); 161.1 (*s*, C=O); 159.4 (*s*, $(PhCH_2NH)_2C$=); 151.5 (*s*, C(2) of furan); 145.1 (*d*, C(5) of furan); 135.8 (br., 2 arom. C); 128.2, 127.7, 127.6, 127.6 (4*d*, 8 arom. CH); 114.6 (*d*, C(3) of furan); 114.3 (*s*, $=C(NO_2)C$); 111.2 (*d*, C(4) of furan); 40.8–40.2 (br., 2 CH_2); 15.1 (*q*, MeS). CI-MS: 451 (9, $[M + 1]^+$), 433 (6), 421 (26), 420 (100), 403 (12), 400 (14), 399 (52), 387 (9), 379 (11), 378 (43), 372 (13), 369 (17), 362 (8), 361 (28), 345 (14), 344 (56), 343 (52), 339 (11), 327 (10), 326 (39), 319 (8), 314 (9), 311 (8), 310 (9), 309 (26), 308 (18), 307 (88), 298 (8), 297 (8), 294 (8), 291 (9), 285 (9), 284 (26), 282 (8), 279 (8), 277 (13), 276 (16), 275 (96), 273 (8). Anal. calc. for $C_{23}H_{22}N_4O_4S$ (450.52): C 61.32, H 4.92, N 12.44, S 7.12; found: C 61.31, H 5.16, N 12.25, S 7.39.

3. *Synthesis of the '3-(Acylamino)-3-amino-2-nitroacrylonitriles'* (**8**). *General Procedure*. To a well stirred soln. of 0.65 mmol of **2** in 2.6 ml DMF, 1.95 mmol (621 mg) of $Hg(OAc)_2$ were added. After 1–2 h (TLC monitoring) the precipitated white solid (MeSHgOAc) was filtered off and washed with small portions of DMF. The DMF solns. were poured into an ice-water mixture and the solid that precipitate was filtered off, washed with H_2O and dried over P_2O_5 *in vacuo*. The amides **8** were purified by column chromatography using CH_2Cl_2.

3.1. N-*[2-Cyano-1-(methylamino)-2-nitroethenyl]*-N-*methylbenzamide* (**8a**). 1.44 g (85%). Colorless crystals. M.p. 192.0–192.5°. IR: 3220*m*, 3210 (sh), 3030 (sh), 2990*w*, 2925*w*, 2205*s*, 1685*s*, 1610*s*, 1575 (sh), 1550 (sh), 1535 (sh), 1480*s*, 1460 (sh), 1450*s*, 1445 (sh), 1425*s*, 1395*s*, 1365*s*, 1320*s*, 1310 (sh), 1295 (sh), 1280*s*, 1230*s*, 1195*s*, 1180*s*, 1160*m*, 1135*w*, 1115*w*, 1060*s*, 1020*m*, 1000*w*, 990*w*, 965*w*, 920*m*, 860*w*, 805*m*, 790*m*, 760*m*, 710*s*, 690*s*, 670*w*, 615*w*, 605*w*. ^{1}H-NMR: 10.29 (br., NH); 7.5–7.35 (*m*, 5 arom. H); 3.34 (br., MeN); 3.24 (*s*, MeN). ^{13}C-NMR[4]): 168.3 (*s*, C=O); 159.7 (*s*, $(MeNH)_2C$=); 133.7 (*s*, 1 arom. C); 132.1, 128.6, 127.1 (3*d*, 5 arom. CH); 113.1 (*s*, $=C(NO_2)CN$); 102.4 (*s*, CN); 33.4, 32.1 (2*q*, 2 MeN). CI-MS: 279 (16), 278 (100), 261 (< 1, $[M + 1]^+$), 246 (8), 245 (54), 230 (8), 229 (8), 216 (5), 202 (11), 153 (7), 125 (6), 123 (7), 118 (7). Anal. calc. for $C_{12}H_{12}N_4O_3$ (260.20): C 55.39, H 4.63, N 21.53; found: C 55.26, H 4.42, N 21.46.

3.2. N-*[2-Cyano-1-(methylamino)-2-nitroethenyl]*-N-*methylfuran-2-carboxamide* (**8b**). 927 mg (57%). Colorless crystals. M.p. 177.9–178.9°. IR: 3250*s*, 3140*m*, 3120*m*, 2950*w*, 2210*s*, 1675*s*, 1620*s* (br.), 1580*s*, 1495*s*, 1480*s*, 1445*s*, 1420 (sh), 1400*s*, 1380*s*, 1365*s*, 1335*s*, 1285*s*, 1245*s*, 1230*m*, 1200*s*, 1185*s*, 1140*m*, 1130 (sh), 1080 (sh), 1060*s*, 1020*s*, 960*w*, 910*s*, 890*m*, 860*w*, 840*m*, 805*m*, 780*s*, 760*m*, 750*m*, 720*m*, 630*w*, 610*w*. ^{1}H-NMR: 10.51 (br., NH); 7.64 (br. *s*, H–C(5) of furan); 7.15 (br. *s*, H–C(3) of furan); 6.54 (*dd*, *J*(4,3) = 3.3, *J*(4,5) = 1.7, H–C(4) of furan); 3.21 (*s*, 2 MeN). ^{13}C-NMR: 159.5 (*s*, C=O); 156.6 (*s*, $(MeNH)_2C$=); 147.3 (*d*, C(5) of furan); 145.5 (*s*, C(2) of furan); 118.4 (*d*, C(3) of furan); 112.6 (*d*, *s*, C(4) of furan, $=C(NO_2)CN$); 101.7 (*s*, CN); 34.6, 31.6 (2*q*, 2 MeN). CI-MS: 269 (13), 268 (100), 251 (< 1, $[M + 1]^+$), 235 (39), 220 (6). Anal. calc. for $C_{10}H_{10}N_4O_4$ (250.22): C 48.00, H 4.03, N 22.39; found: C 48.14, H 4.06, N 22.26.

3.3. N-*[2-Cyano-2-nitro-1-(2-phenylethylamino)ethenyl]*-N-*(2-phenylethylamino)benzamide* (**8c**). 1.32 g (46%). Colorless crystals. M.p. 162.1–162.2°. IR: 3240 (br.), 3030*w*, 2930*w*, 2870*w*, 2210*m*, 1680*s*, 1615*s*, 1605 (sh), 1500*m*, 1470 (sh), 1450*s*, 1440*m*, 1425*m*, 1375*s*, 1350*m*, 1340*m*, 1330*m*, 1320*m*, 1290*s*, 1280*s*, 1270*s*, 1255 (sh), 1235*m*, 1215*m*, 1200 (sh), 1170*m*, 1160 (sh), 1140 (sh), 1130*m*, 1090*w*, 1075*w*, 1030*w*, 1010*w*, 960*w*, 930*w*, 795*w*, 760*m*, 740*w*, 720*m*, 700*s*, 685 (sh), 630*w*. ^{1}H-NMR: 10.18 (br., NH); 7.4–7.2 (*m*, 15 arom. H); 3.97 (br., 3 H,

[4]) Duplication of signals (170.1, 161.2, 134.0, 131.6, 127.2, 114.0, 98.4, 34.1, 32.4).

2 CH_2N); 3.61 (br., 1 H, CH_2N); 3.1–2.95 (*m*, 2 CH_2). ^{13}C-NMR[5]): 170.1 (*s*, C=O); 158.1 (*s*, $(PhCH_2CH_2NH)_2C=$); 138.0, 137.7, 137.3 (3*s*, 3 arom. C); 134.2, 133.6, 131.9, 129.2, 128.6, 127.7, 127.2, 126.7 (8*d*, 12 arom. CH); 113.5 (*s*, $=C(NO_2)CN$); 103.3 (*s*, CN); 48.8, 47.2, 33.9, 33.0 (4*t*, 4 CH_2). CI-MS: 459 (20), 458 (71), 441 (11, $[M + 1]^+$), 426 (7), 425 (20), 411 (5), 410 (7), 409 (17), 407 (12), 396 (9), 394 (9), 382 (11), 355 (11), 354 (48), 337 (19), 322 (5), 321 (20), 306 (6), 305 (25), 304 (9), 303 (37). Anal. calc. for $C_{26}H_{24}N_4O_3$ (440.51): C 79.89, H 5.49, N 12.72; found: C 70.72, H 5.47, N 12.52.

3.4. *N-[2-Cyano-2-nitro-1-(2-phenylethylamino)ethenyl]-N-[(2-phenylethyl)amino]furan-2-carboxamide* (**8d**). 2.0 g (71%). Colorless crystals. M.p. 126.9–128.3°. IR: 3240*w*, 3200*w*, 3120*w*, 3060*w*, 3020*w*, 2920*w*, 2210*m*, 1665*s*, 1615*s* (br.), 1575*s*, 1560 (sh), 1540*w*, 1500*s*, 1475*s*, 1455*s*, 1435 (sh), 1380*s*, 1355*s*, 1325*m*, 1310*s*, 1285*s*, 1270*s*, 1255*s*, 1215*s*, 1205*m*, 1180*s*, 1170*s*, 1145*s*, 1090*w*, 1080*w*, 1050*w*, 1040*w*, 1030*w*, 1015*m*, 965*w*, 920*w*, 910*w*, 885*w*, 855*w*, 820*w*, 770*s*, 760*s*, 750*m*, 730*m*, 705*s*, 655*w*, 620*w*, 610*w*. ^{1}H-NMR: 10.40 (br., NH); 7.60 (br. *s*, H–C(5) of furan); 7.2–7.1 (*m*, 10 arom. H, H–C(3) of furan); 6.52 (*dd*, $J(4,3) = 3.5$, $J(4,5) = 1.7$, H–C(4) of furan); 4.05–3.95 (*m*, 1 H, CH_2N); 3.85–3.8 (*m*, 2 H, CH_2N); 3.65–3.55 (*m*, 1 H, CH_2N); 3.1–2.9 (*m*, 2 CH_2). ^{13}C-NMR: 158.0 (*s*, C=O); 156.8 (*s*, $(PhCH_2CH_2NH)_2C=$); 147.2 (*d*, C(5) of furan); 145.4 (*s*, C(2) of furan); 137.6, 137.5 (2*s*, 2 arom. C); 128.9, 128.6, 128.5, 128.5, 126.7, 126.6 (6*d*, 8 arom. CH); 118.6 (*d*, C(3) of furan); 113.0 (*s*, $=C(NO_2)CN$); 112.6 (*d*, C(4) of furan); 102.9 (*s*, CN); 50.6, 46.7, 34.0, 33.3 (4*t*, 4 CH_2). CI-MS: 449 (6), 448 (23), 340 (7), 253 (9), 199 (7), 198 (100), 181 (6), 180 (82). Anal. calc. for $C_{24}H_{22}N_4O_4$ (430.47): C 66.97, H 5.15, N 13.02; found: C 66.86, H 5.15, N 12.82.

3.5. *N-(Benzylamino)-N-[1-(benzylamino)-2-cyano-2-nitroethenyl]benzamide* (**8e**). 1.55 g (58%). Colorless crystals. M.p. 58.0–58.9°. IR: 3230 (br.), 3050*w*, 3010*w*, 2990*w*, 2940*w*, 2205*m*, 1680*s*, 1610*s*, 1580*s*, 1555 (sh), 1540*m*, 1500*s*, 1450*s*, 1445*s*, 1435 (sh), 1425*s*, 1380*s*, 1350*s*, 1315*s*, 1290 (sh), 1265*s*, 1175*s*, 1130*s*, 1075*m*, 1025*w*, 1000*w*, 970 (sh), 950*m*, 920*w*, 845*w*, 820*w*, 790*m*, 755*m*, 710*s*, 695*s*, 675 (sh), 635*w*, 615*w*. ^{1}H-NMR: 10.42 (br., NH); 7.55–7.05 (*m*, 15 arom. H); 5.00 (*m*, CH_2); 4.70 (br., CH_2). ^{13}C-NMR[6]): 170.3 (*s*, C=O); 157.7 (*s*, $(PhCH_2NH)_2C=$); 135.3, 135.2, 134.2 (3*s*, 3 arom. C); 133.9, 133.7, 132.0, 129.6, 128.4, 127.9, 127.2 (7*d*, 15 arom. CH); 113.0 (*s*, $=C(NO_2)CN$); 103.5 (*s*, CN); 51.0, 48.7 (2*t*, 2 CH_2). CI-MS: 431 (27), 430 (100), 414 (7), 413 (28, $[M + 1]^+$), 397 (7), 379 (8), 366 (5), 278 (6), 277 (31), 275 (11). Anal. calc. for $C_{24}H_{20}N_4O_3$ (412.45): C 69.89, H 4.89, N 13.58; found: C 69.71, H 5.14, N 13.85.

3.6. *N-(Benzylamino)-N-[1-(benzylamino)-2-cyano-2-nitroethenyl]furan-2-carboxamide* (**8f**). 1.94 g (74%). Colorless crystals. M.p. 162.4–162.7°. IR: 3250*m*, 3140*m*, 3030*m*, 2990*m*, 2960*w*, 2210*s*, 1670 (sh), 1660*s*, 1615*s* (br.), 1585 (sh), 1570*s*, 1540 (sh), 1495*s*, 1470*s*, 1455*s*, 1435*s*, 1425*s*, 1385*s*, 1375*s*, 1360*s*, 1335*s*, 1320*s*, 1305*s*, 1285*s*, 1260*s*, 1230*m*, 1210*m*, 1185 (sh), 1170*s*, 1140*s*, 1120*s*, 1075*s*, 1050*w*, 1030*m*, 1015*s*, 1000*w*, 975*w*, 965*w*, 955 (sh), 945*w*, 920*w*, 900*s*, 885*m*, 860*w*, 845*w*, 820*w*, 760*s*, 750 (sh), 735*s*, 710*s*, 705*s*, 660*w*, 610*m*. ^{1}H-NMR: 10.62 (br., NH); 7.58 (br. *s*, H–C(5) of furan); 7.5–7.45 (*m*, 2 arom. H); 7.25–7.1 (*m*, 8 arom. H, H–C(3) of furan); 6.51 (*dd*, $J(4,3) = 3.5$, $J(4,5) = 1.8$, H–C(4) of furan); 5.1–4.95, 4.6–4.45 (2*m*, 2 CH_2). ^{13}C-NMR: 157.7 (*s*, C=O); 156.7 (*s*, $(PhCH_2NH)_2C=$); 147.1 (*d*, C(5) of furan); 145.5 (*s*, C(2) of furan); 135.2, 134.0 (2*s*, 2 arom. C); 129.9, 128.8, 128.5, 128.5, 127.7, 127.4 (6*d*, 10 arom. CH); 119.2 (*d*, C(3) of furan); 112.6 (*d*, *s*, C(4) of furan, $=C(NO_2)CN$); 103.2 (*s*, CN); 51.5, 48.5 (2*t*, 2 CH_2). CI-MS: 421 (25), 420 (100); 403 (6, $[M + 1]^+$), 387 (11), 369 (10). Anal. calc. for $C_{22}H_{18}N_4O_4$ (402.41): C 65.67, H 4.51, N 13.92; found: C 65.54, H 4.56, N 13.70.

N-[3,3-Bis(benzylamino)-1-(methylthio)-2-nitroprop-2-enoyl]furan-2-carboxamide (**10f**). Eluted with CH_2Cl_2/MeOH 20:1: 273 mg (10%). Colorless crystals. M.p. 173.3–173.5°. IR: 3270 (br.), 3220 (br.), 3110*m*, 1705*s*, 1640*s*, 1575*m*, 1565 (sh), 1510 (sh), 1480*s*, 1425*m*, 1365*s*, 1350 (sh), 1330 (sh), 1285*s*, 1245*m*, 1220*m*, 1205 (sh), 1160*m*, 1145*m*, 1110*m*, 1090*s*, 1075*s*, 1050*m*, 1025*w*, 1000*m*, 960*w*, 940*w*, 900*w*, 880*w*, 845*w*, 810*w*, 765*m*, 750*m*, 730*m*, 695*m*, 670*m*, 600*w*. ^{1}H-NMR ((D_6)DMSO): 13.15 (*s*, NHCO); 10.16, 9.51 (2 br. *t*, 2 NH); 7.99 (br. *s*, H–C(5) of furan); 7.45–7.25 (*m*, 10 arom. H, H–C(3) of furan); 6.73 (*dd*, $J(4,3) = 3.5$, $J(4,5) = 1.7$, H–C(4) of furan); 4.63 (*d*, $J = 5.9$, CH_2); 4.39 (*d*, $J = 4.9$, CH_2). CI-MS: 285 (17), 284 (100)[7]), 268 (14), 250 (7). Anal. calc. for $C_{22}H_{20}N_4O_5$ (420.43): C 62.85, H 4.79, N 13.33; found: C 63.02, H 4.82, N 13.62.

4. *N-[3,3-Bis(methylamino)-1-morpholino-2-nitroprop-2-enylidene]benzamide* (**11**). To a suspension of 1.62 mmol (500 mg) of **2a** in 3.2 ml of acetone, 1.62 mmol (0.14 ml) of morpholine were added. The mixture was stirred under reflux overnight. The resulting precipitate was filtered off and washed with acetone: 506 mg (90%) **11**. Pale-yellow needles. M.p. 197.0–197.6° (EtOH). IR: 3260*s*, 3210 (sh), 3080 (sh), 3040 (sh), 2960*m*, 2940*m*, 1710*w*,

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[5]) Duplication of signals (168.5, 159.3, 114.2, 99.0, 50.33, 50.27).

[6]) Duplication of signals (168.8, 158.3, 114.1, 99.0, 52.1).

[7]) The molecule is cleaved even by CI-MS; *m/z* 284 corresponds to the nitroketene-aminal fragment +1.

1630*s*, 1600*s*, 1570*s*, 1560 (sh), 1545*s*, 1525*s*, 1495 (sh), 1485 (sh), 1460 (sh), 1445 (sh), 1420*s*, 1400*s*, 1385 (sh), 1340*s*, 1315*s*, 1290*s*, 1275*s*, 1260*s*, 1245 (sh), 1210*s*, 1185*s*, 1175*s*, 1155*s*, 1130*s*, 1110 (sh), 1100*s*, 1070*s*, 1060*s*, 1030*s*, 1015*s*, 995 (sh), 975*s*, 920*s*, 890*s*, 850*m*, 830*w*, 795*s*, 775 (sh), 755*m*, 705*s*, 680*s*, 670*s*, 630*m*, 610*m*, 600*m*. ^{1}H-NMR ((D$_6$)DMSO): 8.31 (br., 2 NH); 7.94 (*d*, *J* = 8.4, 2 arom. H); 7.5–7.4 (*m*, 3 arom. H); 3.68 (*d*, *J* = 4.5, 2 CH_2O); 3.59 (br. *s*, 2 CH_2N); 2.70, 2.72 (2*s*, 2 CH_3). ^{13}C-NMR: 174.3 (*s*, C=O); 158.8 (*s*, $(MeNH)_2C$=); 157.6 (*s*, C=N); 137.0 (*s*, 1 arom. C); 131.3, 128.8, 127.9 (3*d*, 5 arom. CH); 103.5 (*s*, $=C(NO_2)C$); 65.6 (*t*, 2 CH_2O); 45.8 (*t*, 2 CH_2N); 29.6 (*q*, 2 MeNH). CI-MS: 349 (19), 348 (100, $[M + 1]^+$), 330 (11), 301 (9), 249 (6), 248 (38), 244 (7), 221 (6). Anal. calc. for $C_{16}H_{21}N_5O_4$ (347.38): C 55.32, H 6.09, N 20.16; found: C 55.13, H 6.12, N 20.03.

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