Reactions of 3-alkylsulfanyl-2-arylazo-3-(1-azacycloalk-1-yl)acrylonitriles with maleimide

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Reactions of 2-arylazo-3-(1-azacycloalk-1-yl)-3-methylsulfanylacrylonitriles with maleimide in benzene gave octahydropyrrolo[3,4-*a*]pyrrolizines **2a**—**c**, decahydro-2,7a-diazacyclopenta[*a*]indene **2e**, and decahydro-5-oxa-2,7a-diazacyclopenta[*a*]indene **2f** as a result of 1,3-dipolar cycloaddition. In a similar reaction with 3-allylsulfanyl-2-arylazo-3-(1-azacycloalk-1-yl)acrylonitriles **3**, dipolar cycloaddition and intramolecular cyclization competed to give a mixture of compounds **2** (major products) and 1,4,6,7,8,8a-hexahydropyrrolo[2,1-*c*]-1,2,4-triazines **4b**—**d**, 1,6,7,8,9,9a-hexahydro-4*H*-pyrido[2,1-*c*]-1,2,4-triazine **4e**, and 1,4,6,7,9,9a-hexahydro-1,4-oxazino[3,4-*c*]-1,2,4-triazine **4f** (minor products).

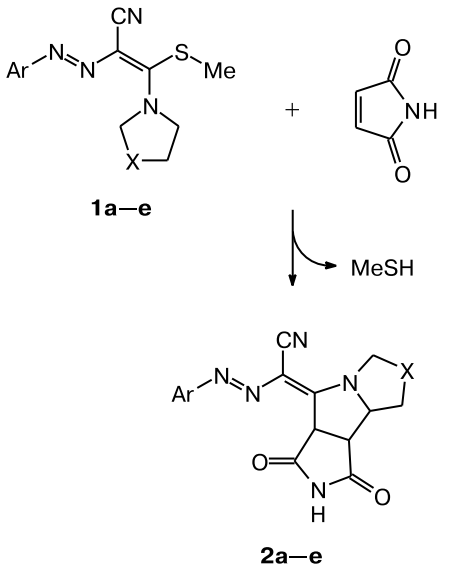
Key words: 1,2-diaza-1,3-butadienes, pyrrolidine, piperidine, morpholine, maleimide, 1,3-dipolar cycloaddition, intramolecular cyclization.

1,2-Diazabuta-1,3-dienes easily react with various dienophiles to give pyridazines (hetero-Diels—Alder reaction).[1] Earlier,[2,3] we have found that the presence of terminal *S*-alkyl- and 1-azacycloalkyl groups in a diazadiene system radically changes the chemical properties of these compounds. 3-Alkylsulfanyl-2-arylazo-3-(pyrrolidin-1-yl)acrylonitriles react as latent dipoles to give products of intramolecular and intermolecular cyclization. The goal of the present work was to study the influence of the structure of the starting compounds on their tendency toward 1,3-dipolar cycloaddition with maleimide, determine the scope of the earlier discovered transformations, and obtain new heterocyclic compounds.

Reactions of 2-arylazo-3-(1-azacycloalk-1-yl)-3-methylsulfanylacrylonitriles **1a**—**e** with an excess of maleimide were carried out in benzene at 50 °C (Scheme 1). The products were isolated by filtration or by liquid chromatography. Structures **2** were determined from spectroscopic and X-ray diffraction data.

The IR spectra of tricyclic compounds **2a**—**c**,**e** show absorption bands at 2200 cm^{-1} (CN) and 1705—1710 cm^{-1} (stretching vibrations of two CO groups). The ^1H NMR spectra of the pyrrolo[3,4-*a*]pyrrolizines **2** obtained contain a double set of signals of all proton-containing groups. The most characteristic signals indicating the formation of cycloadducts **2a**—**c**,**e** are two doublets at δ 4.7—5.20 (1 H, J = 8.5—8.8 Hz), two doublets of doublets at δ 3.6—3.8 (J = 8.5—8.8 Hz, J = 10.0—10.3 Hz), a doublet of triplets at δ 4.4—4.8, and a broadened singlet at δ 11.52—11.7 (NH proton of the pyrrole ring). The number of the protons of the azacycloalkane fragment is reduced by unity,

Scheme 1



Compound	X	Ar	Compound	X	Ar
1a, **2a**	CH_2	4-$NO_2C_6H_4$	**1d**, **2d**	CH_2	4-$MeOC_6H_4$
1b, **2b**	CH_2	2-$CF_3C_6H_4$	**1e**, **2e**	$(CH_2)_2$	4-$NO_2C_6H_4$
1c, **2c**	CH_2	4-ClC_6H_4			

Reagents and conditions: benzene, 50 °C.

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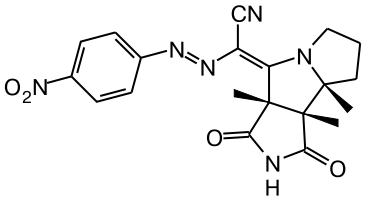
all the signals for this fragment being shifted downfield. Their multiplicity and positions suggest the participation of this fragment in the transformation under study. The structures of products **2** were convincingly confirmed, and some of their structural features were revealed, by single-crystal X-ray diffraction study of product **2b**. The general view of its molecule is shown in Fig. 1; selected bond lengths and bond angles are listed in Table 1.

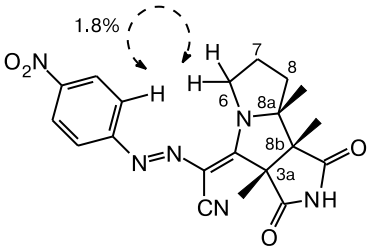
The presence of a system of conjugated double bonds in structure **2b** results in substantial deviations of their lengths from standard values. For instance, the length of the formally single N(2)—C(8) bond is nearly equal to the length of the double C(8)—C(16) bond (1.3859(16) and 1.3864(17) Å); the single bonds C(9)—C(8) and C(1)—N(1) are close in length (1.4264(19) and 1.4242(17) Å, respectively) and are substantially shorter than normal single bonds. The conjugation system N(4)C(9)C(16)C(8)N(2)N(1) is planar: the deviations of the atoms from the mean-square plane do not exceed 0.01 Å. The benzene ring makes an angle of 24.4° with the conjugation plane. According to X-ray diffraction data, 1,3-dipolar cycloaddition yields an *endo*-adduct, namely, the *E*-isomer of pyrrolopyrrolizine **2b**.

The presence of a double set of signals for the proton-containing groups in the ^{1}H NMR spectra of tricyclic cycloadducts **2** suggest that these compounds exist as two isomers about the exocyclic double C=C bond. The 2D NOESY spectrum of compound **2a** shows a cross peak of the *ortho*-proton of the aromatic ring and a proton at the C(6) atom of the pyrrolidine fragment, which is possible only in the *Z*-isomer of this compound.

It should be noted that the yields of cycloadducts **2** decrease considerably with strengthening of the electron-donating properties of the substituent in the aromatic ring. We failed to isolate a product of a reaction of maleimide



2a (*E*-isomer)



2a (*Z*-izomer)

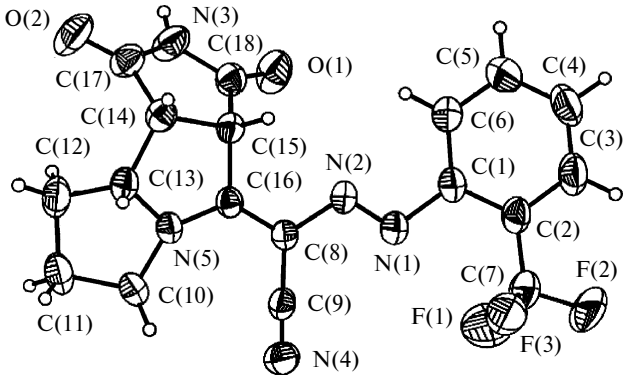


Fig. 1. Structure **2b** with atomic thermal displacement ellipsoids (50% probability) from X-ray diffraction data.

with compound **1d** containing the electron-donating methoxy group (Table 2).

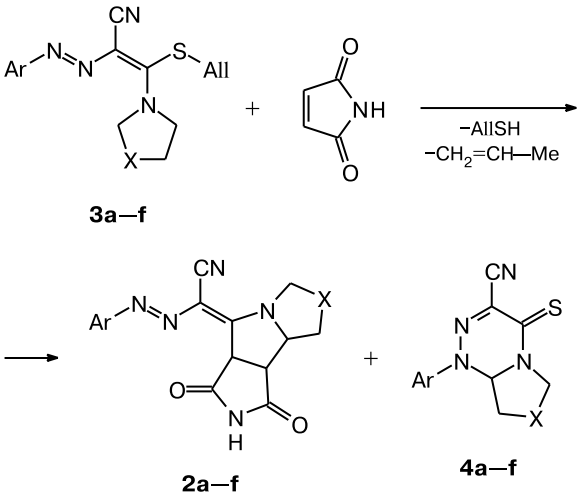
Reactions with *S*-allyl derivatives of 2-arylazo-3-(1-azacycloalk-1-yl)acrylonitriles (**3a—f**) gave minor products along with pyrrolo[3,4-*a*]pyrrolizines **2a—f** (Scheme 2, see Table 1). The compounds obtained were separated by liquid chromatography and identified as pyrrolotriazines **4b—d**, 1,6,7,8,9,9a-hexahydro-4*H*-pyrido[2,1-*c*]-1,2,4-triazine **4e**, and 1,4,6,7,9,9a-hexahydro-[1,4]oxazino[3,4-*c*]-1,2,4-triazine **4f** using spectroscopic techniques.

The formation of bicyclic triazines **4** in the transformations of 3-allylsulfanyl-2-arylazo-3-(1-azacycloalk-1-yl)acrylonitriles in various solvents have been noted earlier.[3] With strengthening of the electron-donating properties of the substituent in the aromatic ring of the starting reagents **3a—d**, the content of intramolecular cyclization products **4** in the reaction mixture increases, while the

Table 1. Selected bond lengths (*d*) and bond angles (ω) in structure **2b**

Bond length	*d*/Å	Angle	ω/deg
N(1)—N(2)	1.2675(14)	C(16)—N(5)—C(10)	132.64(11)
N(1)—C(1)	1.4242(17)	N(1)—N(2)—C(8)	115.55(11)
N(2)—C(8)	1.3859(16)	N(2)—N(1)—C(1)	112.11(11)
N(5)—C(16)	1.3143(15)	N(2)—C(8)—C(16)	116.68(11)
N(5)—C(10)	1.4670(17)	N(2)—C(8)—C(9)	120.43(11)
N(5)—C(13)	1.4654(17)	N(5)—C(10)—C(11)	102.84(11)
N(4)—C(9)	1.1434(16)	N(5)—C(16)—C(8)	128.19(12)
O(2)—C(17)	1.1977(17)	N(5)—C(16)—C(15)	108.61(11)
O(1)—C(18)	1.1952(17)	N(4)—C(9)—C(8)	177.62(15)
N(3)—C(18)	1.3719(19)	O(1)—C(18)—N(3)	124.47(15)
N(3)—C(17)	1.371(2)	O(1)—C(18)—C(15)	128.77(14)
C(2)—C(7)	1.484(2)	O(2)—C(17)—N(3)	124.96(16)
F(3)—C(7)	1.334(2)	O(2)—C(17)—C(14)	127.58(15)
F(2)—C(7)	1.3233(17)	N(3)—C(18)—C(15)	106.75(13)
F(1)—C(7)	1.327(2)	N(3)—C(17)—C(14)	107.44(13)
C(8)—C(16)	1.3864(17)		
C(8)—C(9)	1.4264(19)		

Scheme 2



Compound	X	Ar	Compound	X	Ar
3a, **4a**	CH_2	4-$NO_2C_6H_4$	**3d**, **4d**	CH_2	4-$MeOC_6H_4$
3b, **4b**	CH_2	2-$CF_3C_6H_4$	**3e**, **4e**	$(CH_2)_2$	4-$NO_2C_6H_4$
3c, **4c**	CH_2	4-ClC_6H_4	**2f**, **3f**, **4f**	OCH_2	4-$NO_2C_6H_4$

Reagents and conditions: benzene, 50 °C.

yields of pyrrolopyrrolizines **2** decrease (see Table 2). As with the S-methyl derivative, we did not isolate a cycloadduct of 3-allylsulfanyl-2-(4-methoxyphenylazo)-3-(pyrrolidin-1-yl)acrylonitrile **3d** with maleimide (the corresponding pyrrolopyrrolizine **2d**).

Thus, the reactions of 3-alkylsulfanyl-2-arylazo-3-(1-azacycloalk-1-yl)acrylonitriles **1** and **3** with maleimide follow the 1,3-dipolar cycloaddition mechanism leading to octahydropyrrolo[3,4-*a*]pyrrolizines **2a**—**d**, 1,3-dioxodecahydro-2,7a-diaza- and 1,3-dioxodecahydro-5-oxa-2,7a-diazacyclopenta[*a*]indenes **2e**,**f**, similar to the earlier discovered reactions with *N*-methyl- and *N*-phenylmaleimides. However, the cycloaddition with maleimide proceeds more slowly than that with its N-substituted derivatives; the reaction rate becomes comparable with the rate of an alternative reaction (intramolecular cyclization). The structures of the starting reagents **1** and **3** are crucial for the efficiency of 1,3-dipolar cycloaddition. Introduction of electron-donating substituents into the aromatic ring or replacement of the pyrrolidine substituent by the piperidine/morpholine fragment lowers the yields of cycloadducts but is favorable for the intramolecular cyclization of 3-allylsulfanyl-2-arylazo-3-(1-azacycloalk-1-yl)acrylonitriles, thus increasing the yields of the corresponding fused 1,2,4-triazines **4**.

Table 2. Yields of the products of the reactions of 3-alkylsulfanyl-2-arylazo-3-(1-azacycloalk-1-yl)acrylonitriles **1** and **3** with maleimide

1, **3**	Yield (%)	
	2	**4**
1a	70	0
3a	75	0
1b	57	0
3b	54	TLC*
1c	55	0
3c	35	20
1d	TLC*	0
3d	TLC*	30
1e	44	0
3e	22	40
3f	38	16

* These products were detected using TLC: for compound **2d**, R_f 0.35 (ethyl acetate); for compound **4b**, R_f 0.65 (chloroform—acetone, 30 : 1).

Experimental

^1H and ^{13}C NMR spectra were recorded on Bruker WM-250 and Bruker AVANCE II 400 instruments (250.13 and 400.00 MHz (^1H) and 100.00 MHz (^{13}C)) in DMSO-d_6 with Me_4Si as the internal standard. IR spectra were recorded on a UR-20 spectrometer (in KBr pellets). Mass spectra were measured on a Varian MAT 311A instrument (EI, 70 eV). The course of the reactions was monitored and the purity of the compounds obtained was checked by TLC on Sorbfil UV-254 plates in ethyl acetate, chloroform—acetone (30 : 1), and chloroform—hexane—acetone (5 : 4 : 1). Products were separated and purified by liquid chromatography on silica gel (0.035—0.070 mm, 60 Å, Acros Organics).

3-Alkylsulfanyl-2-arylazo-3-(1-azacycloalk-1-yl)acrylonitriles **1** and **3** were prepared as described earlier.[1] The structures of pyrrolotriazines **4b**—**d** were confirmed by comparing their physicochemical characteristics with those of authentic samples.[3]

Preparation of compounds 2a—f (generat procedure). A solution of 3-alkylsulfanyl-2-arylazo-3-(1-azacycloalk-1-yl)acrylonitrile **1** or **3** (0.5 mmol) and maleimide (0.145 g, 1.5 mmol) in benzene was kept at 50 °C for 7—40 h (TLC). The solvent was removed under reduced pressure and the residue was separated by liquid chromatography with chloroform—hexane—acetone (5 : 4 : 1) as an eluent.

2-(1,3-Dioxooctahydropyrrolo[3,4-*a*]pyrrolizin-4-ylidene)-2-(4-nitrophenylazo)acetonitrile (2a), m.p. 236—238 °C, R_f 0.26 (ethyl acetate). IR, ν/cm^{-1}: 2960 (CH_2); 2200 (CN); 1720 (CO). ^1H NMR, δ: 11.76, 11.66 (both s, 1 H, NH); 8.29, 7.70, 8.28, 7.91 (AA′XX′ and AA′XX′, 4 H, Ar, J = 9.3 Hz); 5.19, 4.85 (both d, 1 H, CH, J = 8.4 Hz); 4.65—4.56 (m, 1 H, CH); 3.92—3.76 (m, 2 H, CH); 3.73, 3.70 (both dd, 1 H, CH, J = 8.4 Hz, J = 9.7 Hz); 2.31—2.13 (m, 2 H, CH_2); 2.08—1.98 (m, 1 H, CH); 1.57—1.39 (m, 1 H, CH). The mixture of the *cis*- and *trans*-isomers in a ratio of 1 : 1. ^{13}C NMR, δ: 176.6 (CO); 174.7 (CO); 174.6 (CO); 173.8 (CO); 161.3 (C_{Ar}); 158.0 (C_{Ar}); 157.7 (C(4)); 157.1 (C(4)); 146.5 (C_{Ar}); 146.4 (C_{Ar}); 136.1 (C_{Ar}); 125.9 (C_{Ar}); 125.6 (C_{Ar}); 123.0 (C_{Ar}); 122.7 (C_{Ar}); 115.2 (CN); 114.9 (CN); 105.9 (C(2′)); 104.5 (C(2′)); 72.0 (C(8a)); 71.6 (C(8a)); 60.0 (C(3a)); 59.9 (C(3a)); 50.1 (C(6)); 46.8 (C(6)); 42.3 (C(8b)); 41.9 (C(8b)); 27.9 (C(7)); 27.7 (C(7)); 27.3 (C(8)); 27.1 (C(8)). MS, m/z (I_{rel} (%)): 366 $[M]^+$ (25.5). Found (%): C, 55.69; H, 3.79; N, 22.75. $C_{17}H_{14}N_6O_4$. Calculated (%): C, 55.74; H, 3.85; N, 22.94.

2-(1,3-Dioxooctahydropyrrolo[3,4-*a*]pyrrolizin-4-ylidene)-2-(2-trifluoromethylphenylazo)acetonitrile (2b), m.p. 296—298 °C,

R_f 0.30 (ethyl acetate). IR, ν/cm^{-1}: 2960 (CH_2); 2195 (CN); 1710 (CO). ^{1}H NMR, δ: 11.80, 11.65 (both s, 1 H, NH); 7.98 (d, 1 H, Ar, J = 7.8 Hz); 7.77 (dd, 1 H, Ar, J = 8.4 Hz, J = 9.7 Hz); 7.68 (dd, 1 H, Ar, J = 7.8 Hz, J = 15.6 Hz); 7.53 (d, 1 H, Ar, J = 7.8 Hz); 7.45 (dd, 1 H, Ar, J = 7.8 Hz, J = 15.6 Hz); 5.17, 4.81 (both d, 1 H, CH, J = 8.3 Hz); 4.61—4.52 (m, 1 H, CH); 3.88—3.65 (m, 3 H, CH); 2.30—2.13 (m, 2 H, CH_2); 2.07—1.97 (m, 1 H, CH); 1.51—1.38 (m, 1 H, CH). The mixture of the *cis*- and *trans*-isomers in a ratio of 5 : 6. MS, m/z (I_{rel} (%)): 389 [M]$^+$ (15.7). Found (%): C, 55.47; H, 3.57; N, 17.79. $C_{18}H_{14}F_3N_5O_2$. Calculated (%): C, 55.53; H, 3.62; N, 17.99.

2-(4-Chlorophenylazo)-2-(1,3-dioxooctahydropyrrolo[3,4-*a*]-pyrrolizin-4-ylidene)acetonitrile (2c), m.p. 273—275 °C, R_f 0.36 (ethyl acetate). IR, ν/cm^{-1}: 2960 (CH_2); 2195 (CN); 1720 (CO). ^{1}H NMR, δ: 11.70, 11.50 (both s, 1 H, NH); 7.74 (d, 1 H, Ar, J = 8.6 Hz); 7.53 (d, 1 H, Ar, J = 8.6 Hz); 7.45—7.34 (m, 2 H, Ar); 5.09, 4.76 (both d, 1 H, CH, J = 8.2 Hz); 4.59—4.45 (m, 1 H, CH); 3.89—3.62 (m, 3 H, CH); 2.39—2.15 (m, 2 H, CH_2); 2.15—1.99 (m, 1 H, CH); 1.59—1.38 (m, 1 H, CH). The mixture of the *cis*- and *trans*-isomers in a ratio of 2 : 3. ^{13}C NMR, δ: 175.9 (CO); 175.8 (CO); 174.0 (CO); 173.2 (CO); 159.4 (C_{Ar}); 154.9 (C_{Ar}); 151.6 (C(4)); 151.3 (C(4)); 132.2 (C_{Ar}); 131.9 (C_{Ar}); 129.2 (C_{Ar}); 128.9 (C_{Ar}); 123.2 (C_{Ar}); 122.9 (C_{Ar}); 114.8 (CN); 114.5 (CN); 103.8 (C(2′)); 102.5 (C(2′)); 70.4 (C(8a)); 69.9 (C(8a)); 58.6 (C(3a)); 58.4 (C(3a)); 48.9 (C(6)); 45.9 (C(6)); 41.6 (C(8b)); 41.3 (C(8b)); 26.9 (C(7)); 26.8 (C(7)); 26.6 (C(8)); 26.4 (C(8)). MS, m/z (I_{rel} (%)): 355 [M]$^+$ (23.5). Found (%): C, 57.32; H, 3.91; N, 19.55. $C_{17}H_{14}ClN_5O_2$. Calculated (%): C, 57.39; H, 3.97; N, 19.68.

2-(1,3-Dioxo-2,7a-diazadecahydrocyclopenta[*a*]inden-8-ylidene)-2-(4-nitrophenylazo)acetonitrile (2e), m.p. 220—222 °C, R_f 0.48 (ethyl acetate). ^{1}H NMR, δ: 11.66, 11.58 (both s, 1 H, NH); 8.24, 7.82, 8.24, 7.66 (AA′XX′ and AA′XX′, 4 H, Ar, J = 8.8 Hz); 5.30, 4.89 (both d, 1 H, CH, J = 12.4 Hz); 5.20, 4.69 (both d, 1 H, CH, J = 9.2 Hz); 4.24 (dt, 1 H, CH_2, J = 11.6 Hz, J = 2.8 Hz); 3.78, 3.73 (both dd, 1 H, CH, J = 9.6 Hz, J = 10.4 Hz); 3.45—3.32 (m, 1 H, CH_2); 2.17—2.08 (m, 1 H, CH_2); 1.99—1.92 (m, 1 H, CH_2); 1.90—1.83 (m, 1 H, CH_2); 1.68—1.57 (m, 2 H, CH_2); 1.37—1.28 (m, 1 H, CH_2). The mixture of the *cis*- and *trans*-isomers in a ratio of 3 : 7. MS, m/z (I_{rel} (%)): 380 [M]$^+$ (10.2). Found (%): C, 56.93; H, 4.36; N, 21.99. $C_{18}H_{16}N_6O_4$. Calculated (%): C, 56.84; H, 4.24; N, 22.09.

2-(1,3-Dioxo-5-oxa-2,7a-diazaoctahydrocyclopenta[*a*]-inden-8-ylidene)-2-(4-nitrophenylazo)acetonitrile (2f), m.p. 269—271 °C, R_f 0.35 (ethyl acetate). ^{1}H NMR, δ: 11.66, 10.79 (both s, 1 H, NH); 8.25, 7.88, 8.25, 7.70 (AA′XX′ and AA′XX′, 4 H, Ar, J = 8.8 Hz); 5.14, 5.01 (both d, 1 H, CH, J = 12.8 Hz); 4.69—4.59 (m, 1 H, CH_2); 4.35—4.23 (m, 1 H, CH_2); 4.22—4.11 (m, 1 H, CH_2); 4.02—3.91 (m, 1 H, CH_2); 3.83, 3.79 (both dd, 1 H, CH, J = 9.6 Hz, J = 10.0 Hz); 3.68—3.53 (m, 2 H, CH_2); 3.39—3.27 (m, 1 H, CH_2). The mixture of the *cis*- and *trans*-isomers in a ratio of 1 : 2. MS, m/z (I_{rel} (%)): 380 [M]$^+$ (10.2). Found (%): C, 53.63; H, 3.76; N, 21.83. $C_{17}H_{14}N_6O_5$. Calculated (%): C, 53.41; H, 3.69; N, 21.98.

1-(4-Nitrophenyl)-4-thioxo-1,6,7,8,9,9a-hexahydro-4*H*-pyrido[2,1-*c*]-1,2,4-triazine-3-carbonitrile (4e), m.p. 132—134 °C, R_f 0.88 (chloroform—acetone, 30 : 1). ^{1}H NMR, δ: 8.28, 7.75 (AA′XX′, 4 H, Ar, J = 9.2 Hz); 6.49 (dd, 1 H, CH, J = 10.8 Hz, J = 2.0 Hz); 5.05 (ddd, 1 H, CH_2, J = 12.8 Hz, J = 2.4 Hz, J = 2.0 Hz); 3.42 (dt, 1 H, CH_2, J = 12.4 Hz, J = 2.8 Hz); 2.17—2.05 (m, 2 H, CH_2); 2.02—1.95 (m, 1 H, CH_2); 1.86—1.73 (m, 2 H, CH_2); 1.72—1.65 (m, 1 H, CH_2). MS, m/z (I_{rel} (%)): 315 [M]$^+$ (52.1). Found (%): C, 53.57; H, 4.28; N, 22.15. $C_{14}H_{13}N_5O_2S$. Calculated (%): C, 53.32; H, 4.16; N, 22.21.

1-(4-Nitrophenyl)-4-thioxo-1,4,6,7,9,9a-hexahydro-[1,4]-oxazino[3,4-*c*]-1,2,4-triazine-3-carbonitrile (4f), m.p. 232—234 °C, R_f 0.6 (chloroform—acetone, 30 : 1). ^{1}H NMR, δ: 8.29, 7.75 (AA′XX′, 4 H, Ar, J = 9.6 Hz); 6.64 (dd, 1 H, CH, J = 10.0 Hz, J = 2.8 Hz); 5.10 (d, 1 H, CH_2, J = 11.2 Hz); 4.00 (dd, 1 H, CH_2, J = 11.2 Hz, J = 10.4 Hz); 3.93—3.87 (m, 1 H, CH_2); 3.83 (dd, 1 H, CH_2, J = 10.8 Hz, J = 2.4 Hz); 3.76—3.68 (m, 2 H, CH_2). MS, m/z (I_{rel} (%)): 317 [M]$^+$ (46.3). Found (%): C, 49.43; H, 3.57; N, 22.30. $C_{13}H_{11}N_5O_3S$. Calculated (%): C, 49.21; H, 3.49; N, 22.07.

X-ray diffraction analysis of compound **2b** was carried out according to a standard procedure at 295(2) K on an Xcalibur 3 automatic four-circle diffractometer equipped with a CCD detector (λ(Mo-K), graphite monochromator, ω scan mode, scan step 1.0°, crystal—detector distance 50 mm). No absorption correction was applied because of negligible absorption. The structure was solved by the direct methods with the SHELXS97 program[4] and refined by the SHELXL97 program[5] by the least-squares method in the anisotropic (isotropic for H atoms) full-matrix approximation on F^2. The hydrogen atoms were located from a difference electron-density map and refined using a riding model with dependent thermal parameters. The H(3) atom at the N(3) atom was refined independently. The X-ray diffraction

Table 3. Crystallographic parameters and the data collection statistics for compound **2b**

Parameter	Value
Molecular formula	$C_{18}H_{14}F_3N_5O_2$
Molecular weight	389.34
Temperature/K	295(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	15.3784(17)
b/Å	7.6382(8)
c/Å	16.519(2)
α/deg	90
β/deg	116.624(12)
γ/deg	90
V/Å^3	1734.6(4)
Z	4
d_{calc}/g cm^{-3}	1.491
μ/mm^{-1}	0.123
Scan range/deg	$2.96 \le \theta \le 28.29$
Scan completeness (%)	98.8
Number of measured reflections (R_{int})	4257 (0.0354)
Number of reflections with $I > 2\sigma(I)$	2356
Number of parameters refined	257
S	1.000
R_1 (for $I > 2\sigma(I)$)	0.0423
wR_2 (for $I > 2\sigma(I)$)	0.0839
R_1 (for all reflections)	0.0957
wR_2 (for all reflections)	0.0922
Residual electron density/e Å^{-3}, ρ_{max}/ρ_{min}	0.202/−0.172

data obtained have been deposited with the Cambridge Crystallographic Data Center (CCDC No. 726 716) and can be made available free upon request on *www.ccdc.cam.ac.uk/data_request/cif*www.ccdc.cam.ac.uk/data_request/cif. Selected crystallographic parameters and the data collection statistics for compound **2b** are summarized in Table 3. Selected bond lengths and bond angles in structure **2b** are given in Table 1.

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References

1. O. A. Attanasi, L. De Crescentini, P. Filippone, F. Mantellini, R. Perrulli, S. Santeusanio, *ARKIVOC*, 2002, 274.
2. T. G. Deryabina, N. P. Belskaia, M. I. Kodess, W. Dehaen, S. Toppet, V. A. Bakulev, *Tetrahedron Lett.*, 2006, **47**, 1853.
3. N. P. Belskaia, T. G. Deryabina, A. V. Koksharov, M. I. Kodess, W. Dehaen, A. T. Lebedev, V. A. Bakulev, *Tetrahedron Lett.*, 2007, **48**, 9128.
4. G. M. Sheldrick, *SHELXS97, Program for the Solution of Crystal Structure*, University of Göttingen, Göttingen, Germany, 1997.
5. G. M. Sheldrick, *SHELXL97, Program for the Refinement of Crystal Structure*, University of Göttingen, Göttingen, Germany, 1997.

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