Exceptional Products of the Desulfurization of *N*,2-Diaryl-5-(arylimino)-2,5-dihydro-4-nitroisothiazol-3-amines[1])

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The desulfurization of several *N*,2-diaryl-5-(arylimino)-2,5-dihydro-4-nitroisothiazol-3-amines **5** with Ph_3P led to complex mixtures of products in low yields. For instance, quinoxaline-2-carboxamide 1-oxides of type **6** (*Scheme 2*) and, in some cases, also 3-nitroquinolines of type **7** (*Scheme 5*) were isolated. By the desulfurization of the substituted derivatives **5b**–**e**, a rearrangement of the intermediates yielded **6** and **7** with a different substitution pattern from that expected from the starting materials (*Scheme 3*). The additional formation of two isomeric 1,2,5-oxadiazole-3-carboxamides **8** was observed only in the case of **5d** ($R^1 = R^2 = F$) (*Scheme 6*). Under the same reaction conditions, the major product of the desulfurization of **5c** was the quinoxaline-2-carboxamide 1-oxide **9** (*Scheme 7*). Reaction mechanisms involving intermediate ketene imines and O transfer from the NO_2 group to the neighboring ketene imine are proposed. The structures of **6a**, **6e**, **6k**, **7b**, and **8d** were established by X-ray crystallography, while the structure of **9** was elucidated by 2D-NMR spectroscopy and corroborated by X-ray crystallography.

1. Introduction. – The desulfurization of several S-containing organic compounds leads to the formation of reactive ketene imines[3]) (*cf.* refs. in [2]) which have proved useful intermediates in heterocyclic chemistry [3–8]. Thus, iminoketene imines **1**, obtained principally by desulfurization of 3-aminoprop-2-enethioamides **2** [9] and by S-extrusion from isothiazole derivatives **3** [10][11], have been used as C_3N synthons for the preparation of heterocycles [7–9] (*Scheme 1*).

Recently, we have reported on the desulfurization of the 3,3-diamino-2-nitroprop-2-enethioamides **2** ($R^2 = RNH$, $R^3 = NO_2$, see *Scheme 1*) [12–14]. This reaction yielded nitroketene imines **1** with an amidino group, which were expected to be useful intermediates for the synthesis of different nitro-substituted compounds. Addition of isocyanates, isothiocyanates, and isonitriles to the heterocumulene system could lead to new heterocycles *via* cycloadditions, and the intramolecular nucleophilic attack of the amino group ($R^2 = RNH$) was expected to give 1,2-dihydro-3-nitroazete **4** ($R^3 = NO_2$). However, all attempts to prepare the desired heterocycles by desulfurization of **2** failed[4]).

The reaction of isothiazol-5(2*H*)-imines **3** with Ph_3P has been described by *Goerdeler et al.* as an efficient method for the synthesis of ketene imines [10]. Taking

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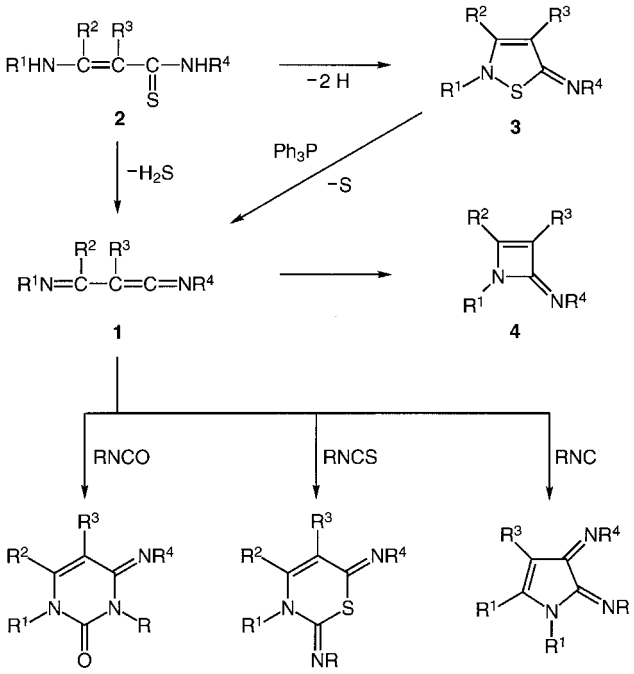
[1]) Presented in part at the 36th IUPAC Congress, Geneva, Switzerland, August 1997.

[2]) Part of the Ph.D. thesis of *D.M.A.*, Universität Zürich, 1998.

[3]) The convenient name ketene imine is used for alk-1-enylidenamines (*cf.* [1]).

[4]) Desulfurization of *S*-methyl 3,3-diamino-2-nitrothioacrylimidates, prepared by methylation of the corresponding 3,3-diamino-2-nitro-thioacrylamides **2**, by means of mercury salts led to intractable mixtures of undefined products.

Scheme 1



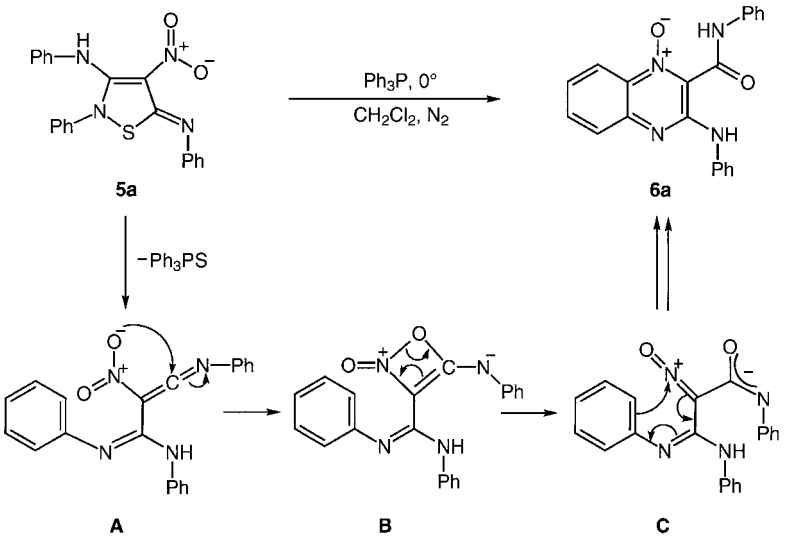
this result into account, we chose 2,5-dihydro-5-imino-4-nitrothiazol-3-amines **3** (R^1, $R^4 = Ar$, $R^2 = ArNH$, $R^3 = NO_2$), prepared by oxidative cyclization of the corresponding prop-2-enethioamide **2** with diethyl azodicarboxylate [13][15], for the same purpose. However, neither the expected nitroketene imines nor the heterocycles depicted in *Scheme 1* could be isolated. On the other hand, the intermediate ketene imine **1** (R^1, $R^4 = Ph$, $R^2 = PhNH$, $R^3 = NO_2$) was successfully trapped by some amines, thiophenol, and benzoic acid [2]. In the absence of these trapping reagents, complex mixtures of several products were formed in low yields. In the present paper, we report on these unexpected results [14], and possible reaction mechanisms are discussed.

2. Results. – 2.1. *Formation of* N-*Aryl-3-(arylamino)quinoxaline-2-carboxamide 1-Oxides* **6**. Treatment of a solution of 2,5-dihydro-4-nitro-*N*,2-diphenyl-5-(phenylimino)isothiazol-3-amine[5]) (**5a**) in absolute CH_2Cl_2 at 0° with Ph_3P led to the formation of 1-oxide **6a** as a minor product, besides many undefined decomposition compounds (*cf.* [14]). A mechanism involving the NO_2 group is proposed, *i.e.* the NO_2 group of intermediate **A** undergoes a nucleophilic addition to the electrophilic C-atom of the ketene imine group which results in an O-transfer (**A** → **B** → **C**; *Scheme 2*); subsequent

[5]) Desulfurization of the corresponding *N*,2-dialkyl derivatives led to intractable mixtures.

electrocyclic ring closure of **C** followed by aromatization leads to **6a**[6]). Although no ketene-imine intermediate could be isolated, in contrast to the reaction with the corresponding isothiazol-5(2*H*)-imines without NO_2 at C(4) and PhNH at C(3) [10], the IR spectra of the reaction mixture showed two strong bands at 2337 and 2261 cm^{-1}, which slowly disappeared during the course of the reaction. The remarkable shift of these IR bands compared with those of simple ketene imines (*ca.* 2000 cm^{-1}) can be explained by the influence of the nitro group (*cf.* [2]).

Scheme 2



The ^{1}H-NMR spectrum of **6a** exhibited two downfield shifted signals assigned to two NH and, in the aromatic region, signals for three nonequivalent benzene rings corresponding to 14 H-atoms. The assignment of the signals was achieved using 2D-NMR spectroscopy, a TOCSY experiment confirming the presence of three different spin systems, namely one disubstituted and two monosubstituted benzene rings. Moreover, in the ^{13}C-NMR spectrum, signals for 14 aromatic CH and seven sp^2 C-atoms were present. Unfortunately, the absence of ^3J(C,H) correlation peaks to some of these C-atoms in the HMBC spectrum did not allow the structure to be established

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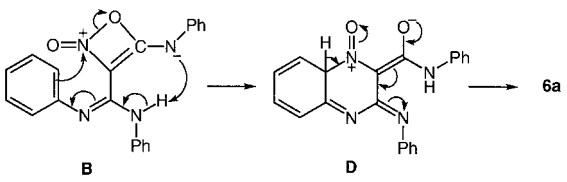
[6]) A direct ring closure of **B** leading to **D** is also conceivable:



unambiguously. The CI-MS of **6a** showed, besides the $[M+1]^+$ peak, $[M+1-16]^+$ as the base peak, which is unusual in the CI-MS of nitro compounds[7]).

After crystallization from CH_2Cl_2, X-ray crystallography established that the product was *N*-phenyl-3-(phenylamino)quinoxaline-2-carboxamide 1-oxide (**6a**) (*Fig. 1*). The amino group of **6a** forms an intramolecular H-bond with the O-atom of the amide CO group (N···O 2.573(2) Å, N–H···O 145(2)°) while the NH of the amide group forms an intramolecular H-bond with the 1-oxide O-atom (N···O 2.541(2) Å, N–H···O 143(2)°). Each interaction has a graph set of S(6) [17]. These H-bonds complete two additional rings within the molecule. The entire molecule is essentially planar with a mean and maximum deviation from the plane of 0.07 and 0.20 Å, respectively. Each Ph group is twisted slightly from this plane, with the *N*-phenyl ring of the amide group and the Ph ring of the phenylamino group making angles of 4.8 and 8.8°, respectively.

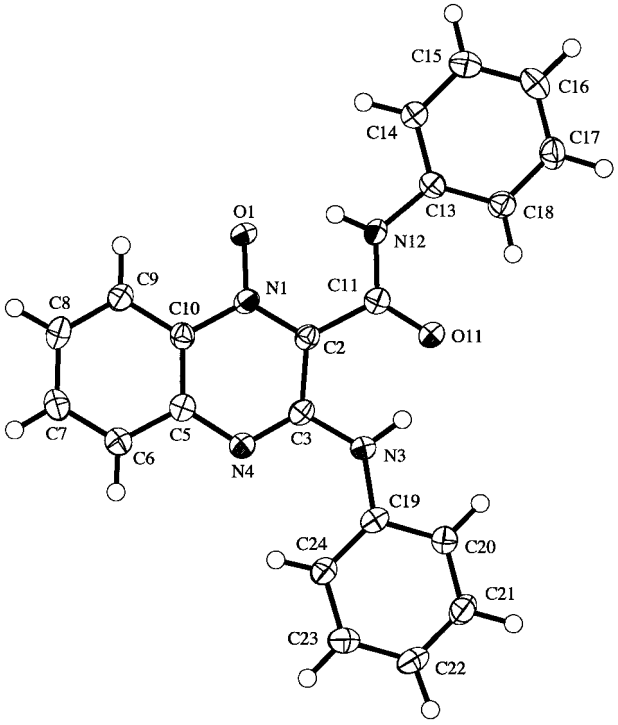


Fig. 1. *ORTEP Plot* [16] *of the molecular structure of* **6a** (arbitrary numbering of the atoms, with 50% probability ellipsoids)

To evaluate the influence of substituents in the Ph groups on the desulfurization, the reaction with Ph_3P was carried out with substituted *N*,2-diaryl-5-(arylimino)-2,5-dihydro-4-nitroisothiazol-3-amines **5b**–**e** (*Table 1*). As established for **5a**, a fast de-

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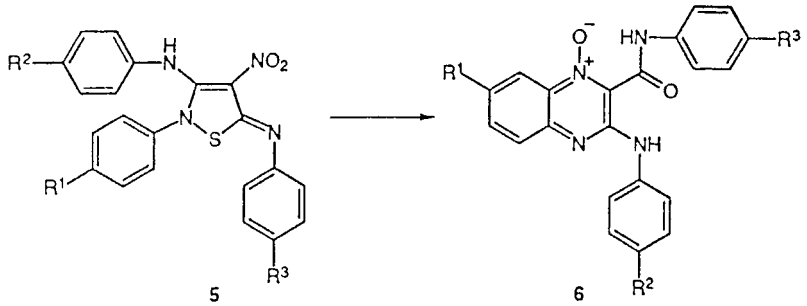
7) In some cases, the $[M+1-30]^+$ peak in the CI-MS points to the presence of a NO_2 group in the compounds.

sulfurization took place in all cases, and a similar reaction behavior was observed (immediate color change from yellow to deep red on Ph_3P addition, *i.e.*, immediate desulfurization; TLC and IR monitoring). In all cases, Ph_3PS was isolated in quantitative yield, thus establishing complete desulfurization of the isothiazole derivatives, and no side reaction of the nitro group with Ph_3P was observed [18]. After preseparation from numerous decomposition products by column chromatography, the *N*-aryl-3-(arylamino)quinoxaline-2-carboxamide 1-oxides **6** were obtained as deep red crystalline materials mixed with Ph_3PS and were purified by repeated MPLC.

Interestingly, the desulfurizations of **5** bearing substituents at the 4-position of the arylimino group (see **5b** and **5c**) or at the 4-position of the aryl group at N(2) and at the

Table 1. *Isolated* N-*Aryl-3-(arylamino)quinoxaline-2-carboxamide 1-Oxides* **6**

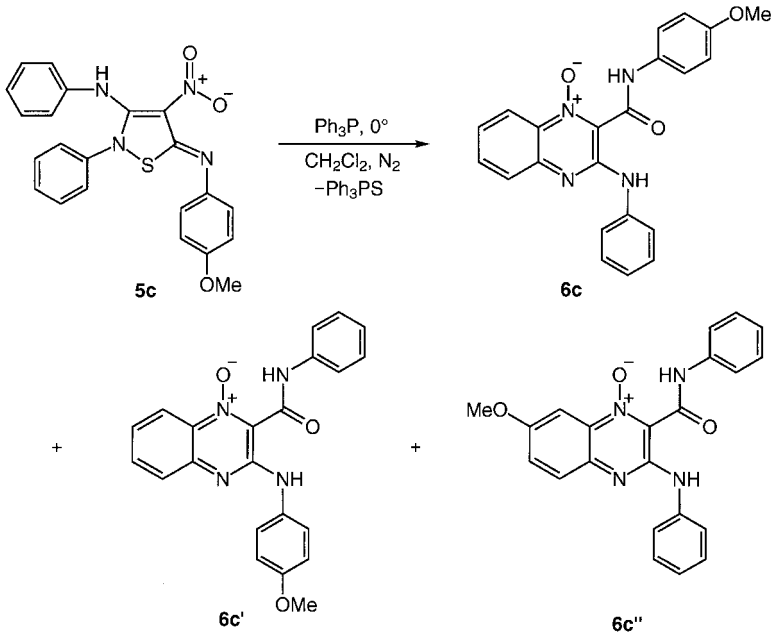


	Product	R^1	R^2	R^3	Yield [%] of **6**
5a	**6a**	H	H	H	10
b	**b**	H	H	NO_2	9
	b′	H	NO_2	H	5
c	**c**	H	H	MeO	2
	c′	H	MeO	H	1
	c″	MeO	H	H	2
d	**d**	F	F	H	7
	d′	H	F	F	2
	d″	F	H	F	2
e	**e**	MeO	MeO	H	5
	e′	MeO	H	MeO	5

amino group at C(3) of the isothiazole ring (see **5d** and **5e**) led to mixtures of two or three isomeric quinoxaline-2-carboxamide 1-oxides **6** (*cf. Scheme 3* for **5c** and *Table 1*). For example, the methoxy derivative **5c** gave the three isomers **6c**, **6c′**, and **6c″**, again in very low yields (*Table 1*). Similar results were observed with **5d**, whereas **5b** and **5e** led to a mixture of only two isomers each. The formation of these isomers can be rationalized by a rearrangement of the intermediate ketene imine (*Scheme 4*). For example, cyclization of the primarily formed ketene imine **A′** ($R^3 = MeO$) as well as that of the tautomeric **A″** according to *Scheme 2* yields quinoxaline-2-carboxamide 1-oxide **6c**. A formal 1,3-shift of the arylamino group of **A′** leads to the rearranged ketene

imine **E**[8]), which, as well as the tautomeric **E′**, in the case of $R^3 = MeO$, can cyclize to give **6c″** and **6c′**, respectively.

Scheme 3



The structures of **6b**–**e′** were deduced from the spectral data and by comparison of the ^{13}C-NMR signals of the respective compounds with those of **6a** (*Table 2*). Although the spectroscopic data of all 1-oxides **6** are very similar, the rearranged products could be detected in the mixture by means of NMR spectroscopy. For instance, the ^{13}C-NMR spectra of **6e** and **6e′** show no remarkable differences (*Table 2*, *cf. Exper. Part*), and in the ^{1}H-NMR spectra, apparently only a slight shifting of all signals is observed. However, closer examination of the NOESY spectra reveals that the most downfield-shifted signal (*ca.* 13.9 ppm) of **6e** corresponds to the NH of an amide group bearing the unsubstituted Ph group, whereas in **6e′** the amide NH correlates with a 4-methoxy-substituted aryl group.

After crystallization of the two isomers **6e** and **6e′** from CD_2Cl_2, the structures of both compounds were corroborated by X-ray crystallography (*Fig. 2*), therefore confirming

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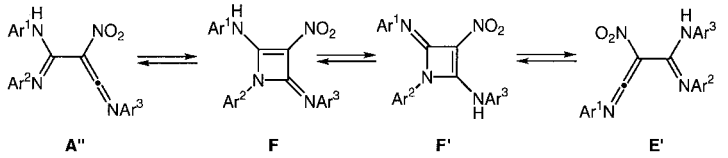
[8]) An energetically conceivable reaction mechanism for the interconversion **A′**/**A″** ⇌ **E**/**E′** is the reversible electrocyclic ring closure to **F** ⇌ **F′** (see, *e.g.*, [19]). We thank the reviewer for this valuable suggestion.



Scheme 4

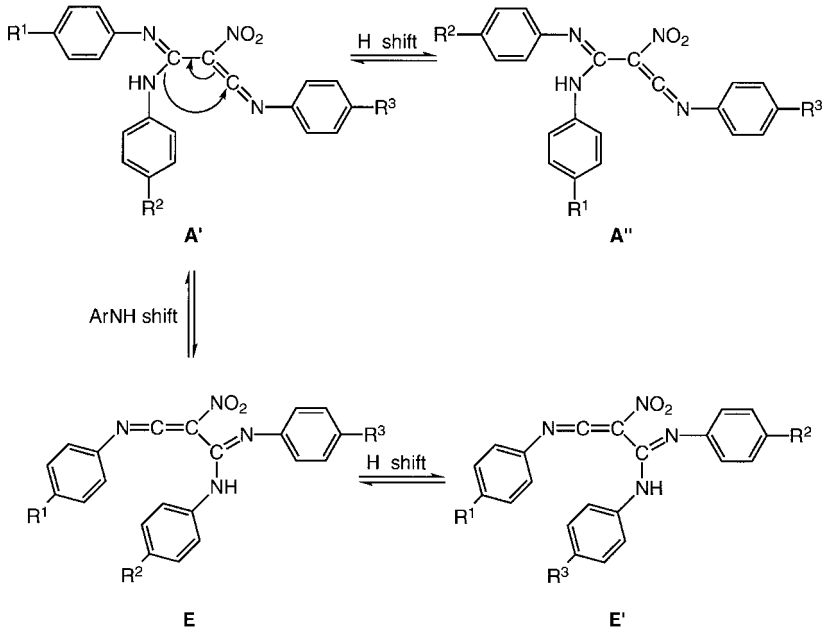


Table 2. *Selected NMR Data of* N-*Aryl-3-(arylamino)quinoxaline-2-carboxamide 1-Oxides* **6**

	^{1}H-NMR δ [ppm]		^{13}C-NMR δ [ppm]					
	NH	NHCO	C(2)	C(3)	C(4a)	C(5)	C(8a)	CO
6a	11.66	13.45	121.1	150.6	142.5	125.5	131.3	159.9
b	11.68	14.26	121.7	151.9	144.1	127.8	132.5	161.9
b′	12.69	13.71	122.6	151.2	144.1	127.8	132.5	161.1
c	12.08	13.69	122.5	152.1	143.7	127.7	132.6	160.9
c′	11.79	13.82	122.0	152.1	143.8	127.4	132.2	161.2
c″	11.82	13.87	121.8	151.1	139.7	129.1	133.1	161.5
d	11.91	13.69	122.4	151.5	140.6	129.6	132.3	160.7
d′	11.96	13.83	121.9	151.8	143.5	127.5	132.4	161.1
d″	11.92	13.74	122.4	151.5	140.7	129.8	132.3	160.8
e	11.61	13.91	121.3	151.1	139.7	128.8	132.6	161.3
e′	11.90	13.78	121.9	151.0	139.6	129.1	133.0	161.1

the proposed rearrangement. The crystal structures of **6e** and **6e′** are very similar to that of **6a**. Intramolecular H-bonds link the amino group to the O-atom of the amide CO group at C(2)[9]) (N···O 2.598(2) Å, N–H···O 142(2)° for **6e**; N···O 2.582(2) Å, N–H···O 146(2)° for **6e′**) and the NH of the amide group to the O-atom of the 1-oxide (N···O 2.531(2) Å, N–H···O 148(2)° for **6e**; N···O 2.541(2) Å, N–H···O 144(2)° for **6e′**). These H-bonds complete two additional rings within the molecules.

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

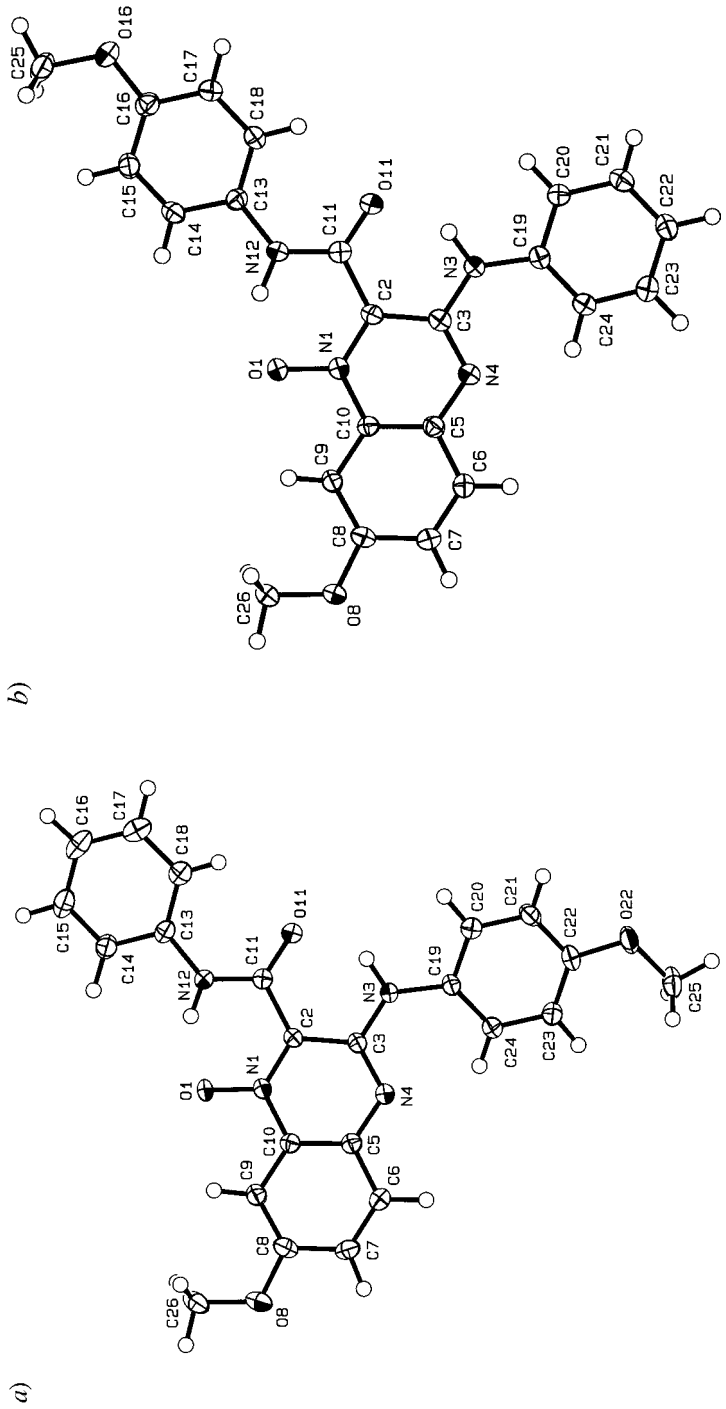
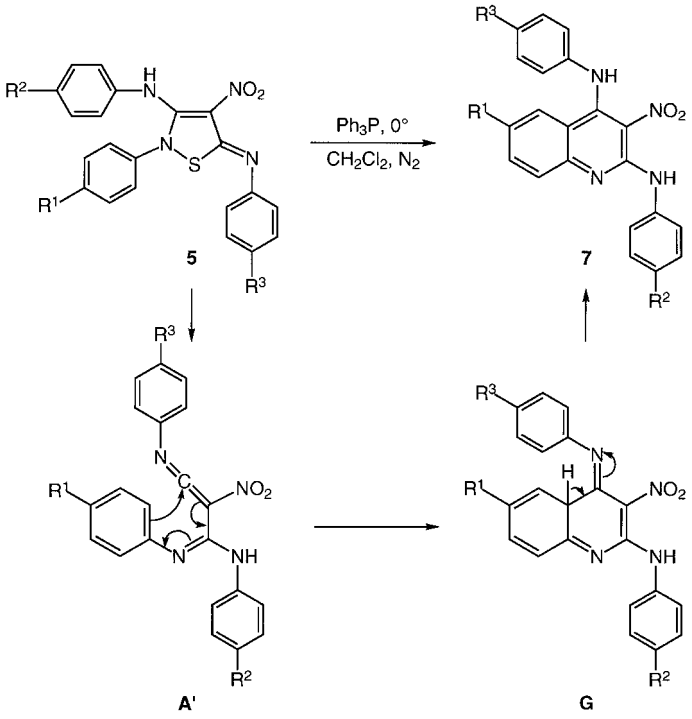


Fig. 2. *ORTEP Plot* [16] *of the molecular structures of* a) **6e** *and* b) **6e′** (arbitrary numbering of the atoms, with 50% probability ellipsoids)

In summary, all 1-oxides were isolated in very low yields (1–10%, *Table 1*), and no significant influence from the substituents could be found. Attempts to improve the yields by changing the solvent[10]) and the reaction conditions failed.

2.2. *Formation of 3-Nitroquinoline-2,4-diamines* **7**. From the product mixtures of the desulfurization of **5b**, **5c**, and **5e** under the conditions described in *Sect. 2.1*, 3-nitroquinolinediamines **7** were isolated as additional products, albeit in low yields (*Scheme 5* and *Table 3*). The proposed mechanism for their formation involves an electrocyclic ring closure of the intermediate unstable nitroketene imine **A′** to give **G** followed by aromatization[11]). The formation of **7c** from **5c** and **7e′** from **5e** indicated again a rearrangement of the intermediate ketene imine as formally indicated in *Scheme 4*.

Scheme 5



Compounds **7** were purified by means of MPLC and characterized by their spectroscopic data. The CI-MS (NH_3 as ionization gas) recorded at 165° show the $[M+1]^+$ and $[M+1-30]^+$ ions which are typical for some nitro compounds. Elucidation of the structures was achieved using principally 2D-NMR spectroscopy,

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[10]) In DMF, no reaction took place, and in MeOH and acetone, yields remained unchanged, even though precipitation of the 1-oxides and Ph_3PS occurred during the reaction.

[11]) The cyclization can also be formulated *via* an electrophilic aromatic substitution of the arylimino moiety with the electrophilic C-atom of the nitroketene imine group.

Table 3. *3-Nitroquinoline-2,4-diamines* **7** *Isolated after Desulfurization of* **5**

	Product	R^1	R^2	R^3	Yield [%] of **7**
5b	**7b**	H	H	NO_2	9
c	**c**	MeO	H	H	2
e	**e**	MeO	MeO	H	4
	e′	MeO	H	MeO	5

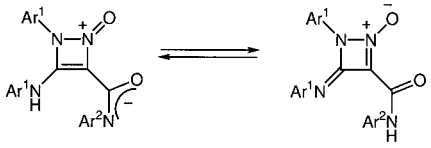
and, in the case of **7b**, the structure was confirmed by X-ray crystallography (*Fig. 3*). The heterocyclic ring of **7b** is slightly distorted from planarity with C(3)[12]) and the N-atom of the NO_2 group showing the greatest deviation from the plane of the bicyclic system. The plane of the NO_2 group is also twisted by *ca.* 43° from the heterocyclic ring plane. These deviations might be the result of steric interactions between the NO_2 group at C(3) and the two adjacent arylamino groups. The phenylamino group at C(2) forms an intramolecular H-bond with one of the O-atoms of the NO_2 group at C(3) ($N\cdots O$ 2.709(2) Å, $N-H\cdots O$ 136(2)°), forming a six-membered ring (graph set S(6) [17]). The NH of the (4-nitrophenyl)amino group at C(4) is involved in an intermolecular H-bond with the other O-atom of the NO_2 group ($N\cdots O$ 3.118(2) Å, $N-H\cdots O$ 158(2)°) of a neighboring molecule. The intermolecular H-bond links the molecules into centrosymmetric dimers (graph set $R_2^2(12)$ [17]) (*Fig. 3*).

2.3. *Formation of* N-*Aryl-4-(arylimino)-5-(4-fluorophenyl)-4,5-dihydro-1,2,5-oxadiazole-3-carboxamides* **8**. Surprisingly, the 1,2,5-oxadiazole derivatives **8d** and **8d′** were isolated from the reaction mixture of the desulfurization of **5d**, in addition to the *N*-oxides **6d**, **6d′**, and **6d″** (*cf. Table 1*). A possible mechanism for the formation of these unexpected compounds consists of an O-transfer from the NO_2 group to the electrophilic C-atom of the ketene imine **A** yielding **C′** (*cf. Scheme 2*) which, *via* nucleophilic attack of the N-atom of the imino group at the O-atom of the NO moiety, yields **8** (*Scheme 6)*[13]). The formation of isomers **8d** and **8d′** from **5d** again supports the assumption of an isomerization of the ketene-imine intermediate (*cf. Scheme 4*).

The 1,2,5-oxadiazole derivatives **8d** and **8d′** were obtained in only 3% yield each after purification by MPLC. The spectroscopic data of both compounds are almost identical. Attempts to elucidate the structure by means of the HMBC spectrum failed due to the absence of ^3J(C,H) correlation peaks to the non-aromatic sp^2 C-atoms. Thus, only the signals corresponding to the aryl, (arylimino), and *N*-aryl substituents could be assigned using 2D-NMR spectroscopy. Finally, after crystallization from CD_2Cl_2/hexane, the structure of **8d** was established by X-ray crystallography (*Fig. 4*). The X-

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

[13]) Another conceivable mechanism for the formation of **8** is the ring closure of **C′** to **H**/**H′** followed by a ring enlargement *via* a 1,2-shift. We thank the reviewer for this suggestion.



H **H′**

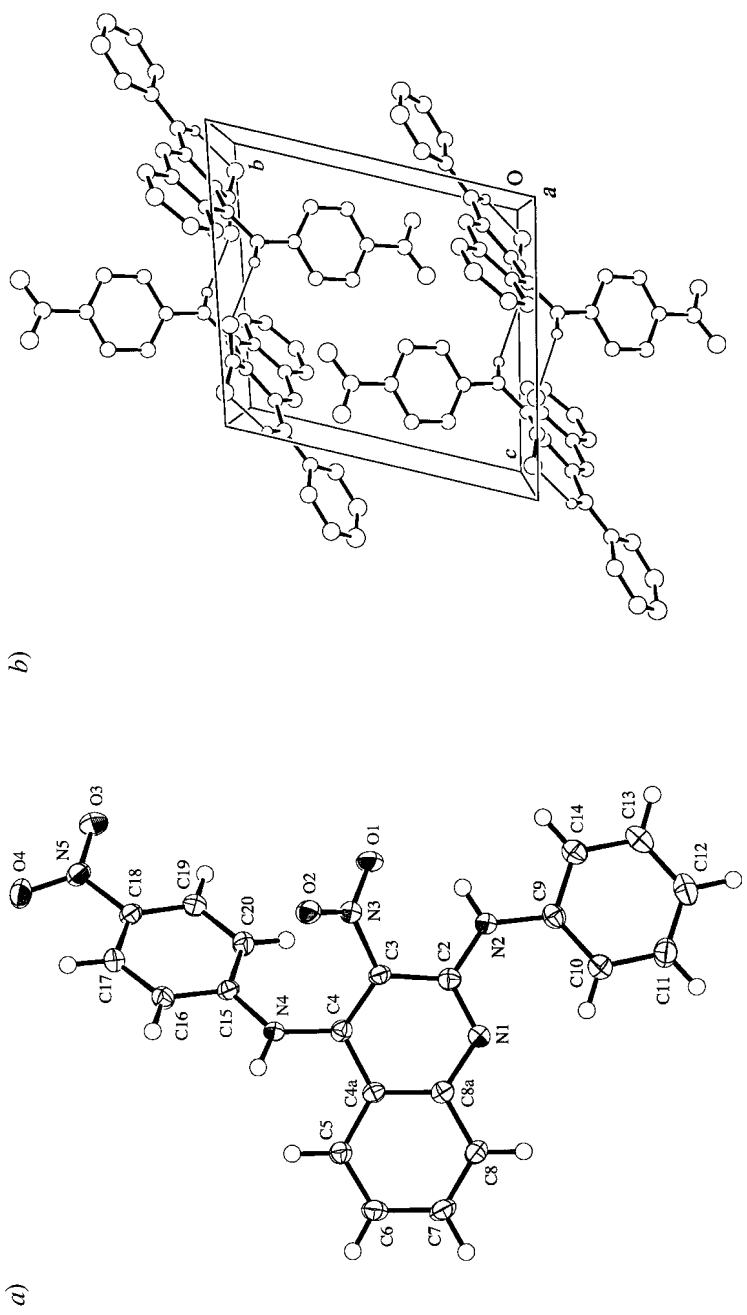
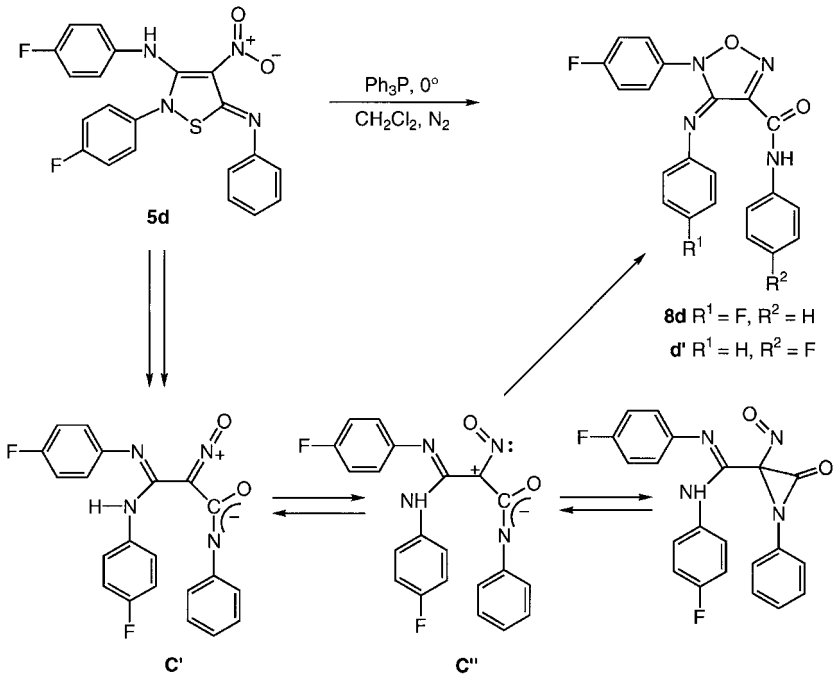


Fig. 3. a) *ORTEP Plot* [16] *of the molecular structure of* **7b** (arbitrary numbering of the atoms, with 50% probability ellipsoids). b) *Molecular packing of* **7b** *showing the H-bonding scheme* (arbitrary spheres for atoms; uninvolved H-atoms omitted for clarity).

Scheme 6



ray analysis of **8d** revealed that the asymmetric unit contains two symmetry-independent molecules. The conformations of these two molecules are quite similar. The main differences between them are small twists of the aryl substituents and a slightly different puckering in the essentially planar five-membered rings. Each

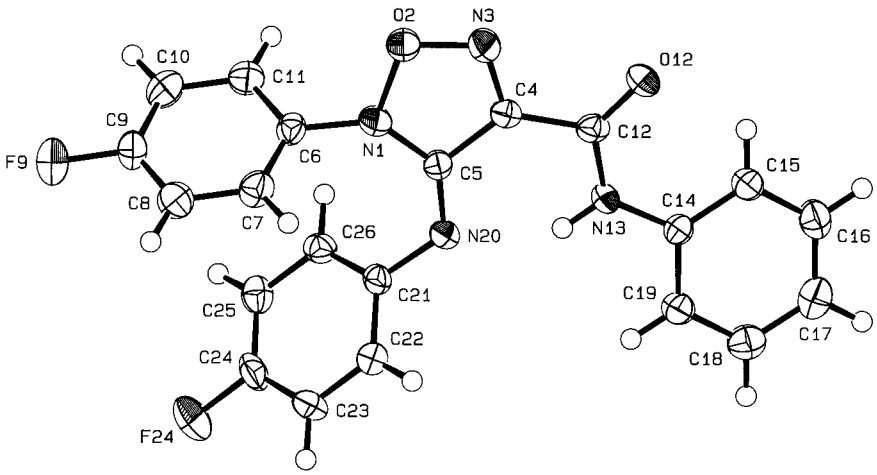
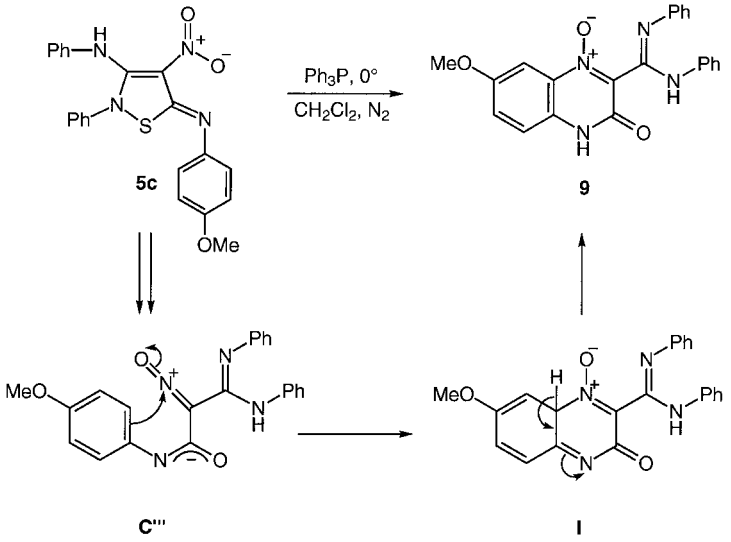


Fig. 4. *ORTEP Plot* [16] *of the molecular structure of one of the symmetry-independent molecules of* **8d** (arbitrary numbering of the atoms, with 50% probability ellipsoids)

molecule forms an intramolecular H-bond between the NH of the amide group and the N-atom of the 4-(fluorophenyl)imino group (N ··· N 2.783(3) Å, N–H ··· N 145(2)° for molecule A; N ··· N 2.768(3) Å, N–H ··· N 146(3)° for molecule B), thus forming a six-membered ring. There are no intermolecular interactions.

2.4. *Formation of 3,4-Dihydro-7-methoxy*-N,N′*-diphenylquinoxaline-2-carboximidamid 1-Oxide* (**9**). Compound **9** was isolated as the major product of the desulfurization of **5c**, besides the 1-oxides **6c** and **6c′** and the nitroquinolinediamine **7c**. Curiously, the IR spectrum of the reaction mixture in this case showed only one absorption band at 2337 cm^{-1} instead of those usually observed at 2261 and 2337 cm^{-1} (*cf. Sect. 2.1*). A mechanism for the formation of **9** similar to that proposed for the 1-oxides **6** would imply cyclization of intermediate **C‴** involving the 4-methoxyphenyl group to give **I**, followed by aromatization (*Scheme 7*).

Scheme 7



After preseparation from the other products by column chromatography, 1-oxide **9** was purified by recrystallization from CH_2Cl_2/hexane. The compound was obtained in 26% yield as bright yellow crystals which decomposed in CH_2Cl_2 solution to unknown red products[14]). The structure of **9** was elucidated from the spectroscopic data.

In the IR spectrum, the absorption bands corresponding to a NO_2 group were absent. In addition, the presence of the base peak $[M+1-16]^+$ in the CI-MS ruled out a nitroquinoline structure of type **7**, pointing to a more likely 1-oxide structure similar to **6**. The main information for the characterization of **9** was obtained from NMR spectroscopy. The ^{1}H-NMR spectrum in (D_6)acetone at 220 K displayed two downfield-shifted signals assigned to two NH groups, and signals for 13 aromatic H-atoms. The TOCSY experiment revealed exchange between the two NH and between the H-atoms of two monosubstituted aryl substituents, making its resolution difficult. However, a third spin system corresponding to a trisubstituted benzene ring was clearly observable. Total signal assignment could be achieved using HSQC and HMBC spectra. The HSQC spectrum exhibited cross peaks for nine different aromatic CH, four of them corresponding to two equivalent CH each. The

[14]) As **9** decomposed in CH_2Cl_2, the solvent used for the reaction, higher yields could not be ruled out.

appearance of strong ^3J(C,H) correlation peaks for the aromatic systems in the HMBC spectrum showed the trisubstitution of one benzene ring, once with the MeO group, and twice with two hetero atoms, as substitution with C-atoms would give rise to further cross peaks. Moreover, the signals for the two monosubstituted benzene rings could also be completely assigned. The NH appearing at *ca.* 9 ppm exhibited two ^3J(C,H) correlation peaks, one to two equivalent aromatic CH showing the connection with one of the benzene rings, and a second one to C(2) of the heterocyclic system. Furthermore, the appearance of a ^2J(C,H) correlation to an aromatic C_{ipso} atom confirmed the bond to a benzene ring, and a second ^2J(C,H) cross peak to the C-atom of the amidino group was also in accordance with the proposed structure. Additionally, a ^4J(C,H) to the aromatic C_{ipso} atom of the phenylimino group was observed. The NH absorbing at *ca.* 11 ppm showed only two ^3J(C,H) correlation peaks[15]), one to C(2) and another one to C(8a) of the quinoxaline structure. Also in accordance with the proposed structure was the low-field shift of this NH, which could be explained by the deshielding effect of the neighboring CO group. Although exchange between the two NH, and also between the two benzene rings, was perceptible in the NOESY as well as in the NOE spectra, it was clearly evident from the NOE difference spectra that one of the NH is connected to the trisubstituted benzene ring. NOE Peaks for the *ortho*-CH of the Ph groups and also for the H-atom at C(5) of the quinoxaline structure were observed. These results are in agreement with the assignment made by means of the HMBC spectrum and support the proposed structure for **9**. The ^{13}C-NMR signals are comparable with those of the similar 1-oxides **6** (*cf. Table 2*).

After crystallization from DMSO, X-ray crystallography confirmed the structure of **9** (*Fig. 5*). Compound **9** crystallized together with DMSO in a 1:1 ratio. Each DMSO molecule accepts intermolecular H-bonds from two different substrate molecules. The phenylamino group and the NH of the heterocyclic ring interact with the O-atom of the DMSO molecules (N···O 2.767(4) Å, N–H···O 168°, N···O 2.827(4) Å, N–H···O 169°) to link the entities into ring systems containing two substrate molecules and two DMSO molecules (graph set $R_4^2(16)$ [17]) (*Fig. 5*).

3. Discussion. – Isothiazol-5(2*H*)-imines of type **3** were reported by *Goerdeler et al.* to be desulfurized with Ph_3P yielding ketene imines **1** [10] or products resulting from their rearrangements [11]. In contrast to these results, *N*-acyl-substituted 4-nitroisothiazol-5(2*H*)-imines **3** ($R^2 = NHR^1$, $R^3 = NO_2$, $R^4 = COR$; see *Scheme 1*) remained unchanged under the reaction conditions[16]) and *N*,2-diaryl-5-(arylimino)-2,5-dihydro-4-nitroisothiazol-3-amines **5a**–**e** led, albeit in low yield, to the unexpected quinoxalinecarboxamide 1-oxides **6**, nitroquinolinediamines **7**, oxadiazolecarboxamides **8**, and the quinoxalinecarboximidamide 1-oxide **9**. Although a ketene imine could not be isolated in any of the cases, we assume that in the first step of the reaction, an intermediate ketene imine of type **A** is formed which further affords the four different types of product obtained (*Schemes 2–7*). The formation of the quinoxaline 1-oxides of type **6** and **9** and the oxadiazoles **8** requires the participation of the nitro group in an O-transfer reaction to the electrophilic C-atom of the intermediate ketene imine.

An intramolecular nucleophilic addition of a nitro-group O-atom to C-atom/hetero atom double bonds has been observed for the first time in the reaction of nitroolefins with enamines [20–22]. Later *O'Bannon et al.* generated nitrocarbenes from 2-diazo-2-nitroacetate by N_2 elimination and detected an O-transfer from the nitro group leading to acyl-nitroso compounds [23]. Moreover, nitroalkenes have been reported to react with ynamines as heterodienes resulting in the incorporation of the nitro group in a [4 + 2]-cycloaddition reaction [24–26]. In a first step, nucleophilic addition of the

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15) Perhaps, the third correlation could not be observed because of line width.

16) Even by using $(Me_2N)_3P$ as the desulfurizing reagent, no reaction took place.

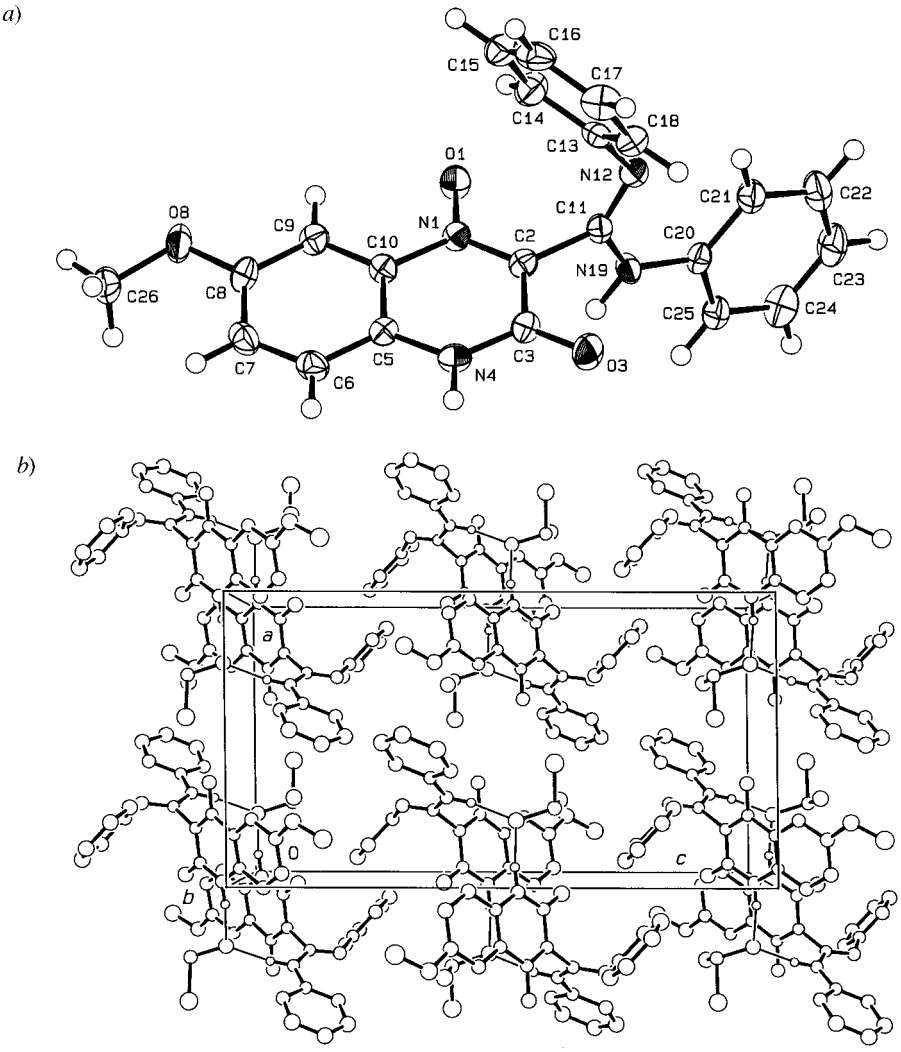

Fig. 5. a) *ORTEP Plot* [16] *of the molecular structure of* **9** (arbitrary numbering of the atoms, with 50% probability ellipsoids). b) *Molecular packing of* **9** *showing the H-bonding scheme* (arbitrary spheres for atoms; uninvolved H-atoms omitted for clarity).

electron-rich acetylene to the nitroalkene yields a 1,4-dipolar ketene-imine derivative which undergoes a cyclization to give a six-membered nitronic ester. Generally, these compounds could not be isolated because the cyloaddition is followed in almost all cases by a fast ring-contraction reaction, which involves simultaneous cleavage of the weak N–O bond and formation of a carbonyl function.

Our results suggest a similar reactivity of the initially formed nitroketene imine **A**, which reacts further to give the nitronic ester **B** (*Scheme 2*). Probably, the nitro group in **A** lies in a favorable position to the ketene imine C-atom which is highly electrophilic

due to the electron-withdrawing effect of the nitro group. Taking into account the intramolecular reaction between nitro and carbodiimide groups [27], the O-transfer to the ketene-imine C-atom can be rationalized in terms of a nucleophilic reaction by neighboring-group participation of the nitro group. *Houghton et al.* proposed a mechanism for this reaction which involves a sequence of electrocyclic ring-closing and -opening reactions that include a stable intermediate which, in solution, showed an IR absorption at 2260 cm^{-1}. This absorption was assigned to an isocyanate group as the tautomeric structure of the isolated intermediate. Regarding the IR bands at 2261 and 2337 cm^{-1} observed in the desulfurization of **5**, the presence of similar species, which in our case lead to numerous decomposition compounds, is conceivable. Furthermore, the absence of the absorption at 2261 cm^{-1} in the IR spectrum of the reaction mixture from **5c** could be explained by the fact that a fast cyclization to **9** did not allow the formation of a tautomeric isocyanate. Only in the reaction mixture from **5c**, this IR band was missing, and in this case, one major product was isolated, namely **9**.

Formally, the O-transfer from the nitro group to the electrophilic C-atom of the intermediate ketene imine could be either a two-step reaction as already discussed (*cf. Scheme 2*), or a concerted process *via* simultaneous formation of the carbonyl function and an NO moiety[17]). A subsequent electrocyclization or an electrophilic aromatic substitution involving the corresponding aryl moiety leads to **6** and **9**, respectively. It is interesting to note that the cyclization with the 4-methoxyphenyl moiety of intermediate **C** to yield **9** occurred faster than the cyclization to give **6**; this may be the result of the electron-donating effect of the 4-methoxy group which activates the benzene ring for the aromatic substitution (*cf. Schemes 2* and *7*). On the other hand, the formation of oxadiazoles **8** from **C** is also reasonable (*Scheme 6*): the amidine N-atom reacts as a nucleophile with the O-atom of the NO group.

As to the oxadiazole derivatives of type **8**, very few have been reported in the literature. Apparently, *N*-substituted derivatives of the 1,2,5-oxadiazole (furazan) system are rather rare in contrast to the well documented synthesis of furazanes[18]). To the best of our knowledge, only bicyclic compounds with a bridgehead N-atom [31][32] and 3,4-ring fusion [33] have been described. Recently, *Sheremetev et al.* [34] reported the synthesis of 2-ethyl-1,2,5-oxadiazol-3(2*H*)-ones, the first non-condensed *N*-substituted 1,2,5-oxadiazoles with a functional group at the ring. The comparable oxadiazole derivatives **8** with *N*-aryl substitution and an imino group were isolated only on desulfurization of **5d** and, so far, it is not clear which factors are decisive for this type of ring closure.

Several syntheses of quinoxaline 1-oxides have been described. Thus, the reaction of benzofurazane oxide with enones and amines [35], the deoxygenation of quinoxaline dioxides with PCl_3 [36], as well as the intramolecular cyclization of 3-(2-nitroanilino)cyclohex-2-enones [37] and *N*-aryl-substituted 2-nitroenamines [38] lead to quinoxaline 1-oxides. A similar compound to the quinoxalinone 1-oxide **9** was isolated

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17) A similar, well-documented reaction is the generation of nitrile oxides from nitro compounds. Suitable starting materials are nitroalkanes [28][29] and arylbromonitromethanes [18], and reagents used for this purpose are acid chlorides and Ph_3P.

18) Furazanes have been synthesized from 1,2-dioximes and their derivatives, as well as from α-hydroxyimides, α-hydroximino azides, α-amino-nitroso compounds, *etc.* [30].

in a small amount by *Toman* and *Klicnar* after the oxidation of a quinoxalinone obtained from an isoxazole derivative and benzene-1,2-diamine [39]. Quinoxaline 1-oxides containing angiotensin II receptor antagonist analogues have been reported to possess very potent biological activity [40]. Therefore, the formation of such a quinoxaline structure in a convenient one-step synthesis starting from easily obtainable nitroisothiazole derivatives **5** [13] is an attractive method. Unfortunately, the scope of this reaction seems to be rather restricted by the low yields which, so far, could not be improved by changing the reaction conditions.

A mechanism similar to that proposed for the formation of the nitroquinolinediamines **7** (*Scheme 5*) has been reported by *Flowers et al.* [41] for the synthesis of *N*-arylquinolin-4-amines from perfluoro-2-methylpent-2-ene and 2-unsubstituted primary arylamines. The products were formed *via* an intramolecular electrophilic aromatic substitution of an arylimino group by the electrophilic C-atom of a ketene imine. This mechanism was supported by the stable ketene imines that were isolated in the case of the reaction with 2-substituted arylamines or *tert*-butylamine where the intramolecular cyclization was hindered. Furthermore, *Molina et al.* have recently described the synthesis of isoquinoline derivatives based on the initial generation of a *N*-vinylketene imine that undergoes a cascade of pericyclic reactions; one of them is also an intramolecular aromatic substitution of an aryl group by the electrophilic C-atom of the ketene imine [42].

We thank the analytical sections of our institute for recording spectra and elemental analyses. Financial support by the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, is gratefully acknowledged. *D.M.A.* thanks the *Swiss Federal Government* for a 'Bundesstipendium'.

Experimental Part

1. *General*. See [2]. TLC: silica gel *60 F_{254}* plates (0.25 mm: *Merck*): CH_2Cl_2/hexane 3:1 and CH_2Cl_2/MeOH 100:5 as eluents. IR Spectra: *Perkin-Elmer-1600 FT-IR* spectrophotometer; in KBr, absorption bands in cm^{-1}. ^{1}H-NMR (600 MHz) and ^{13}C-NMR (150.9 MHz) Spectra: *Bruker AMX-600* instrument in CD_2Cl_2, unless otherwise stated.

2. *Starting Materials*. The amines **5** were prepared according to the general procedures described in [13][15]: *2,5-dihydro-4-nitro-*N,*2-diphenyl-5-(phenylimino)isothiazol-3-amine* (**5a**), *2,5-dihydro-4-nitro-5-[(4-nitrophenyl)imino]-*N,*2-diphenylisothiazol-3-amine* (**5b**), *2,5-dihydro-5-[(4-methoxyphenyl)imino]-4-nitro-*N,*2-diphenylisothiazol-3-amine* (**5c**), N,*2-bis(4-fluorophenyl)-2,5-dihydro-4-nitro-5-(phenylimino)isothiazol-3-amine* (**5d**), and *2,5-dihydro-*N,*2-bis(4-methoxyphenyl)-4-nitro-5-(phenylimino)isothiazol-3-amine* (**5e**).

3. N-*Aryl-3-(arylamino)quinoxaline-2-carboxamide 1-Oxides* **6**: *General Procedure*. To a soln. of **5** (1.2 mmol) in abs. CH_2Cl_2 (7 ml), a soln. of Ph_3P (314 mg, 1.2 mmol) in abs. CH_2Cl_2 (3.2 ml) was added at 0° under N_2. The mixture was stirred at 0° for *ca.* 20 min and then allowed to reach r.t. After 1 h (monitoring by TLC and IR spectroscopy[19])), the very complex mixture was preseparated by CC (CH_2Cl_2/MeOH). Then, the compounds were purified by repeated CC or MPLC (CH_2Cl_2/hexane) and crystallized by slow evaporation of the solvent.

N-*Phenyl-3-(phenylamino)quinoxaline-2-carboxamide 1-Oxide* (**6a**). CC: 42.7 mg (10%). Red crystals. M.p. 181°. Crystallization from CH_2Cl_2 yielded suitable crystals for an X-ray crystal-structure determination. IR: 3073*m*, 2924*w*, 1663*m*, 1592*s*, 1546*s*, 1497*s*, 1484*m*, 1448*s*, 1380*m*, 1369*w*, 1353*w*, 1328*w*, 1285*w*, 1261*w*, 1238*m*, 1217*w*, 1194*w*, 1155*w*, 1137*m*, 1102*w*, 1088*w*, 1071*w*, 1018*w*, 948*w*, 917*w*, 901*w*, 854*w*, 830*w*, 783*w*, 753*s*, 684*m*, 659*m*. ^{1}H-NMR ($CDCl_3$, 318 K): 13.45 (*s*, PhN*H*CO); 11.66 (*s*, PhN*H*); 8.14 (*d*, *J* = 8.6, 1 arom. H); 7.62 (*d*, *J* = 7.1, 2 arom. H); 7.51 (*d*, *J* = 8.6, 2 arom. H); 7.5–7.4 (*m*, 2 arom. H); 7.2–7.15 (*m*, 3 arom. H); 7.13 (*t*, *J* = 8.0,

[19]) The IR spectra showed two bands at 2337 and 2261 cm^{-1} which disappeared slowly. After *ca.* 1 h, the absence of the bands indicated the end of the reaction [2].

2 arom. H); 6.98, 6.86 (2*t*, *J* = 7.4, 2 arom. H). ^{13}C-NMR ($CDCl_3$, 318 K): 159.9 (*s*, CO); 150.6 (*s*, C(3)); 142.5 (*s*, C(4a)); 138.6, 136.2 (2*s*, 2 arom. C); 132.6 (*d*, C(6)); 131.3 (*s*, C(8a)); 128.4, 128.1 (2*d*, 4 arom. CH); 126.6 (*d*, C(7)); 125.5 (*d*, C(5)); 125.0, 122.8 (2*d*, 2 arom. CH); 121.1 (*s*, C(2)); 121.1, 120.4 (2*d*, 4 arom. CH); 118.8 (*d*, C(8)). ESI-MS: 379 ($[M+Na]^+$), 357 ($[M+H]^+$). Anal. calc. for $C_{21}H_{16}N_4O_2$ (356.39): C 70.78, H 4.52, N 15.72; found: C 70.74, H 4.47, N 15.84.

N-*(4-Nitrophenyl)-3-(phenylamino)quinoxaline-2-carboxamide 1-Oxide* (**6b**). CC: 43.3 mg (9%). Red crystals. M.p. 230–231°. IR: 3384*w*, 3242*w*, 3200*w*, 3104*w*, 2924*w*, 1662*m*, 1596*s*, 1544*s*, 1512*s*, 1485*s*, 1445*m*, 1413*m*, 1387*m*, 1371*m*, 1343*s*, 1286*m*, 1236*m*, 1220*m*, 1190*m*, 1139*m*, 1115*m*, 1100*m*, 1087*m*, 1073*m*, 1016*w*, 919*w*, 901*w*, 865*m*, 855*m*, 828*w*, 797*w*, 785*w*, 765*s*, 753*m*, 691*m*, 660*m*. ^{1}H-NMR (300 K): 14.26 (*s*, $NO_2C_6H_4NHCO$); 11.68 (*s*, PhN*H*); 8.40 (*d*, *J* = 8.7, 1 arom. H); 8.28, 7.98 (2*d*, *J* = 9.2, 4 arom. H); 7.88 (*d*, *J* = 7.9, 2 arom. H); 7.8–7.75 (*m*, 2 arom. H); 7.5–7.45 (*m*, 1 arom. H); 7.41, 7.15 (2*t*, *J* = 7.4, 3 arom. H). ^{13}C-NMR (300 K): 161.9 (*s*, CO); 151.9 (*s*, C(3)); 145.0 (*s*, 1 arom. C); 144.1 (*s*, C(4a)); 143.4, 139.6 (2*s*, 2 arom. C); 134.4 (*d*, C(6)); 132.5 (*s*, C(8a)); 129.4 (*d*, 2 arom. CH); 127.8 (*d*, C(5)); 127.2 (*d*, C(7)); 125.5 (*d*, 2 arom. CH); 124.4, 122.0, 121.9 (3*d*, 5 arom. CH); 121.7 (*s*, C(2)); 120.0 (*d*, C(8)). ESI-MS: 424 ($[M+Na]^+$), 402 ($[M+H]^+$).

3-[(4-Nitrophenyl)amino]-N-*phenylquinoxaline-2-carboxamide 1-Oxide* (**6b′**). CC: 24.1 mg (5%). Red-orange crystals. M.p. 201–203°. IR: 3016*m*, 2924*m*, 2862*w*, 1662*m*, 1587*s*, 1544*s*, 1506*s*, 1448*m*, 1412*m*, 1382*m*, 1334*s*, 1292*m*, 1265*m*, 1247*m*, 1222*m*, 1186*m*, 1166*w*, 1141*m*, 1114*s*, 1087*m*, 1073*m*, 918*w*, 866*w*, 842*m*, 830*m*, 788*m*, 761*s*, 750*m*, 688*m*, 661*w*. ^{1}H-NMR (300 K): 13.71 (*s*, PhN*H*CO); 12.69 (*s*, $NO_2C_6H_4NH$); 8.46 (*dd*, *J* = 8.7, 1.0, 1 arom. H); 8.24, 8.13 (2*d*, *J* = 9.2, 4 arom. H); 7.77 (*d*, *J* = 7.9, 2 arom. H); 7.75–7.65 (*m*, 2 arom. H); 7.58 (*td*, *J* = 7.8, 1.3, 1 arom. H); 7.45, 7.26 (2*t*, *J* = 7.4, 3 arom. H). ^{13}C-NMR (300 K): 161.1 (*s*, CO); 151.2 (*s*, C(3)); 146.0 (*s*, 1 arom. C); 144.1 (*s*, C(4a)); 143.0, 137.2 (2*s*, 2 arom. C); 134.4 (*d*, C(6)); 132.5 (*s*, C(8a)); 129.7 (*d*, 2 arom. CH); 127.8 (*d*, C(5)); 127.2 (*d*, C(7)); 126.5, 125.5, 122.5, 120.3 (4*d*, 7 arom. CH); 122.6 (*s*, C(2)); 120.1 (*d*, C(8)). ESI-MS: 424 ($[M+Na]^+$), 402 ($[M+H]^+$).

N-*(4-Methoxyphenyl)-3-(phenylamino)quinoxaline-2-carboxamide 1-Oxide* (**6c**). MPLC: 9.3 mg (2%). Red orange crystals. M.p. 195–196°. IR: 3440 (br.), 3051*m*, 2956*m*, 2830*w*, 1657*m*, 1590*s*, 1544*s*, 1509*s*, 1485*s*, 1449*m*, 1418*w*, 1383*w*, 1371*w*, 1349*w*, 1329*w*, 1298*w*, 1261*m*, 1237*s*, 1194*w*, 1174*m*, 1158*w*, 1139*m*, 1106*w*, 1089*w*, 1074*w*, 1031*m*, 950*w*, 918*w*, 898*w*, 829*m*, 808*w*, 784*m*, 762*s*, 693*w*, 659*m*. ^{1}H-NMR (300 K): 13.69 (*s*, $MeOC_6H_4NHCO$); 12.08 (*s*, PhN*H*); 8.41 (*d*, *J* = 8.5, 1 arom. H); 7.89 (*d*, *J* = 7.6, 2 arom. H); 7.8–7.7 (*m*, 2 arom. H); 7.70 (*d*, *J* = 9.0, 2 arom. H); 7.46 (*td*, *J* = 7.6, 1.9, 2 arom. H); 7.40, 7.12 (2*t*, *J* = 7.4, 3 arom. H); 6.96 (*d*, *J* = 9.0, 2 arom. H); 3.83 (*s*, MeO). ^{13}C-NMR (300 K): 160.9 (*s*, CO); 158.0 (*s*, 1 arom. C); 152.1 (*s*, C(3)); 143.7 (*s*, C(4a)); 140.0 (*s*, 1 arom. C); 133.8 (*d*, C(6)); 132.6 (*s*, C(8a)); 130.5 (*s*, 1 arom. C); 129.3 (*d*, 2 arom. CH); 127.7 (*d*, C(5)); 126.7 (*d*, C(7)); 124.4, 123.8 (2*d*, 3 arom. CH); 122.5 (*s*, C(2)); 121.7 (*d*, 2 arom. CH); 120.0 (*d*, C(8)); 114.8 (*d*, 2 arom. CH); 56.0 (*q*, MeO). ESI-MS: 387 ($[M+H]^+$).

3-[(4-Methoxyphenyl)amino]-N-*phenylquinoxaline-2-carboxamide 1-Oxide* (**6c′**). MPLC: 4.6 mg (1%). Dark red crystals. M.p. 197–199°. IR: 3440 (br.), 3069*m*, 2996*m*, 2956*m*, 2930*m*, 1660*s*, 1611*s*, 1594*s*, 1560*s*, 1510*s*, 1488*s*, 1462*m*, 1449*s*, 1383*m*, 1357*m*, 1321*w*, 1301*m*, 1282*w*, 1253*s*, 1231*s*, 1180*m*, 1165*w*, 1151*m*, 1140*m*, 1103*m*, 1087*m*, 1076*m*, 1035*m*, 1018*w*, 918*w*, 898*w*, 860*w*, 836*m*, 804*m*, 785*m*, 761*s*, 685*m*, 652*m*. ^{1}H-NMR (300 K): 13.82 (*s*, PhN*H*CO); 11.79 (*s*, $MeOC_6H_4NH$); 8.39 (*d*, *J* = 8.5, 1 arom. H); 7.8–7.65 (*m*, 6 arom. H); 7.45–7.4 (*m*, 3 arom. H); 7.23 (*t*, *J* = 7.5, 1 arom. H); 6.94 (*d*, *J* = 9.0, 2 arom. H); 3.82 (*s*, MeO). ^{13}C-NMR (300 K): 161.2 (*s*, CO): 156.4 (*s*, 1 arom. C); 152.1 (*s*, C(3)); 143.8 (*s*, C(4a)); 137.3 (*s*, 1 arom. C); 133.8 (*d*, C(6)); 132.6 (*s*, 1 arom. C); 132.2 (*s*, C(8a)); 129.5 (*d*, 2 arom. CH); 127.4 (*d*, C(5)); 126.3 (*d*, C(7)); 126.0, 123.5, 122.2 (3*d*, 5 arom. CH); 122.0 (*s*, C(2)); 119.8 (*d*, C(8)); 114.2 (*d*, 2 arom. CH); 56.0 (*q*, MeO). ESI-MS: 387 ($[M+H]^+$)[20]).

7-Methoxy-N-*phenyl-3-(phenylamino)quinoxaline-2-carboxamide 1-Oxide* (**6c″**). MPLC: 9.3 mg (2%). Red crystals. M.p. 220–221°. IR: 3123*m*, 2929*m*, 1661*m*, 1592*s*, 1547*s*, 1494*s*, 1442*s*, 1428*m*, 1394*m*, 1371*m*, 1345*w*, 1329*m*, 1277*s*, 1235*w*, 1210*s*, 1177*w*, 1163*m*, 1130*m*, 1090*w*, 1071*w*, 1022*m*, 960*w*, 930*w*, 902*w*, 841*m*, 814*w*, 782*m*, 754*s*, 710*w*, 690*m*. ^{1}H-NMR (300 K): 13.87 (*s*, PhN*H*CO); 11.82 (*s*, PhN*H*); 7.85 (*d*, *J* = 7.5, 2 arom. H); 7.85–7.75 (*m*, 3 arom. H); 7.68 (*d*, *J* = 9.1, 1 arom. H); 7.43 (*t*, *J* = 7.9, 2 arom. H); 7.4–7.35 (*m*, 3 arom. H); 7.23, 7.10 (2*tt*, *J* = 7.4, 1.2, 2 arom. H); 3.96 (*s*, MeO). ^{13}C-NMR (300 K): 161.5 (*s*, CO); 159.4 (*s*, C(7)); 151.1 (*s*, C(3)); 140.2 (*s*, 1 arom. C); 139.7 (*s*, C(4a)); 137.6 (*s*, 1 arom. C); 133.1 (*s*, C(8a)); 129.6, 129.3 (2*d*, 4 arom. CH); 129.1 (*d*, C(5)); 126.7 (*d*, C(6)); 126.0, 123.7, 122.3 (3*d*, 4 arom. CH); 121.8 (*s*, C(2)); 121.5 (*d*, 2 arom. CH); 98.4 (*d*, C(8)); 56.6 (*q*, MeO). ESI-MS: 387 ($[M+H]^+$).

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[20]) In the CI-MS, only the $[M+H-16]^+$ peak was observed.

7-Fluoro-3-[(4-fluorophenyl)amino]-N-*phenylquinoxaline-2-carboxamide 1-Oxide* (**6d**). MPLC: 33.0 mg (7%). Red crystals. M.p. 197–198°. IR: 3428 (br.), 3059*m*, 2923*m*, 2852*w*, 1664*m*, 1613*s*, 1565*s*, 1510*s*, 1495*s*, 1450*s*, 1420*m*, 1388*m*, 1373*m*, 1346*m*, 1264*s*, 1224*s*, 1164*s*, 1124*m*, 1106*m*, 1087*m*, 1074*m*, 972*w*, 932*w*, 904*w*, 864*m*, 826*s*, 800*m*, 779*m*, 751*m*, 712*m*, 684*m*. ^{1}H-NMR (280 K): 13.69 (*s*, PhN*H*CO); 11.91 (*s*, FC_6H_4NH); 8.06 (*dd*, ^3J(H,F) = 9.0, *J* = 3.0, 1 arom. H); 7.80 (*dd*, *J* = 9.1, ^4J(H,F) = 4.9, 2 arom. H); 7.74 (*d*, *J* = 7.8, 2 arom. H); 7.72 (*dd*, *J* = 9.2, ^4J(H,F) = 5.4, 1 arom. H); 7.50 (*td*, *J* = 9.2, 3.0, ^3J(H,F) = 8.0, 1 arom. H); 7.42 (*d*, *J* = 7.5, 2 arom. H); 7.23 (*tt*, *J* = 7.4, 1.1, 1 arom. H); 7.08 (*t*, *J* = 9.1, ^3J(H,F) = 8.6, 2 arom. H). ^{13}C-NMR (280 K): 160.9 (*d*, ^1J(C,F) = 251.9, C(7)); 160.8 (*s*, CO); 159.3 (*d*, ^1J(C,F) = 242.2, 1 arom. C); 151.5 (*s*, C(3)); 140.6 (*s*, C(4a)); 137.1, 135.6 (2*s*, 2 arom. C); 132.3 (*s*, C(8a)); 129.6 (*dd*, ^3J(C,F) = 8.7, C(5)); 129.5, 126.1 (2*d*, 3 arom. CH); 123.8 (*dd*, ^2J(C,F) = 25.6, C(6)); 123.2 (*dd*, ^3J(C,F) = 7.7, 2 arom. CH); 122.4 (*s*, C(2)); 122.1 (*d*, 2 arom. CH); 115.7 (*dd*, ^2J(C,F) = 22.3, 2 arom. CH); 105.0 (*dd*, ^2J(C,F) = 27.9, C(8)). ESI-MS: 393 ($[M+H]^+$). Anal. calc. for $C_{21}H_{14}F_2N_4O_2$ (392.36): C 64.28, H 3.60, N 14.28; found: C 64.53, H 3.82, N 14.10.

N-*(4-Fluorophenyl)-3-[(4-fluorophenyl)amino]quinoxaline-2-carboxamide 1-Oxide* (**6d′**). MPLC: 11.3 mg (2.4%). Red crystals. M.p. 225–226°. IR: 3432 (br.), 3078 (br.), 2924*m*, 2852*m*, 1656*m*, 1604*s*, 1547*s*, 1506*s*, 1448*m*, 1412*m*, 1383*m*, 1370*m*, 1322*w*, 1267*w*, 1227*s*, 1212*m*, 1156*m*, 1143*m*, 1125*w*, 1102*m*, 1081*m*, 1014*w*, 932*w*, 858*w*, 832*m*, 785*w*, 761*m*, 702*w*. ^{1}H-NMR (280 K): 13.83 (*s*, FC_6H_4NHCO); 11.96 (*s*, FC_6H_4NH); 8.40 (*d*, *J* = 8.4, 1 arom. H); 7.85 (*dd*, *J* = 9.1, ^3J(H,F) = 4.9, 2 arom. H); 7.8–7.7 (*m*, 4 arom. H); 7.48 (*td*, *J* = 7.4, 2.4, 1 arom. H); 7.15–7.05 (*m*, 4 arom. H). ^{13}C-NMR (280 K): 161.3 (*s*, CO); 160.6, 159.6 (2*d*, ^1J(C,F) = 244.8, 2 arom. C); 151.8 (*s*, C(3)); 143.5 (*s*, C(4a)); 135.7 (*s*, 1 arom. C); 134.0 (*d*, C(6)); 133.4 (*s*, 1 arom. C); 132.4 (*s*, C(8a)); 127.5 (*d*, C(5)); 126.8 (*d*, C(7)); 124.0, 123.1 (2*dd*, ^3J(C,F) = 8.1, 4 arom. CH); 121.9 (*s*, C(2)); 119.8 (*d*, C(8)); 116.2, 115.8 (2*dd*, ^2J(C,F) = 22.6, 4 arom. CH). ESI-MS: 393 ($[M+H]^+$).

7-Fluoro-N-*(4-fluorophenyl)-3-(phenylamino)quinoxaline-2-carboxamide 1-Oxide* (**6d″**). MPLC: 9.4 mg (2%). Red crystals. M.p. 211–212°. IR: 3428 (br.), 3073*m*, 2923*m*, 2852*m*, 1736*w*, 1664*m*, 1604*s*, 1556*s*, 1510*s*, 1495*s*, 1448*m*, 1414*m*, 1389*m*, 1373*m*, 1340*m*, 1330*m*, 1265*m*, 1227*s*, 1200*m*, 1158*s*, 1124*m*, 1106*m*, 1090*m*, 1073*m*, 974*w*, 899*w*, 870*m*, 849*m*, 830*s*, 779*m*, 753*s*, 704*w*, 689*m*. ^{1}H-NMR (280 K): 13.74 (*s*, FC_6H_4NHCO); 11.92 (*s*, PhN*H*); 8.08 (*dd*, ^3J(H,F) = 9.0, *J* = 3.0, 1 arom. H); 7.84 (*d*, *J* = 7.6, 2 arom. H); 7.8–7.7 (*m*, 3 arom. H); 7.53 (*td*, *J* = 9.2, 3.0, ^3J(H,F) = 8.0, 1 arom. H); 7.39 (*t*, *J* = 7.9, 2 arom. H); 7.15–7.1 (*m*, 3 arom. H). ^{13}C-NMR (280 K): 161.0 (*d*, ^1J(C,F) = 248.5, C(7)); 160.8 (*s*, CO); 160.4 (*d*, ^1J(C,F) = 244.8, 1 arom. C); 151.5 (*s*, C(3)); 140.7 (*s*, C(4a)); 139.5, 133.3 (2*s*, 2 arom. C); 132.3 (*d*, ^4J(C,F) = 11.2, C(8a)); 129.8 (*dd*, ^3J(C,F) = 8.7, C(5)); 129.2, 124.1 (2*d*, 3 arom. CH); 124.0 (*dd*, ^3J(C,F) = 8.1, 2 arom. CH); 123.8 (*dd*, ^2J(C,F) = 25.8, C(6)); 122.4 (*s*, C(2)); 121.6 (*d*, 2 arom. CH); 116.2 (*dd*, ^2J(C,F) = 22.6, 2 arom. CH); 104.9 (*dd*, ^2J(C,F) = 27.9, C(8)). CI-MS: 393 (5, $[M+H]^+$), 377 (100, $[M+H-16]^+$).

7-Methoxy-3-[(4-methoxyphenyl)amino]-N-*phenylquinoxaline-2-carboxamide 1-Oxide* (**6e**). MPLC: 25.0 mg (5%). Dark lilac crystals. M.p. 198–199°. Crystallization from CD_2Cl_2 yielded suitable crystals for an X-ray crystal-structure determination. IR: 3160*w*, 3116*w*, 3068*w*, 3038*w*, 2926*m*, 1656*m*, 1592*s*, 1573*m*, 1538*s*, 1509*s*, 1448*s*, 1429*m*, 1393*m*, 1370*m*, 1338*m*, 1278*s*, 1249*s*, 1208*s*, 1168*m*, 1131*m*, 1086*m*, 1030*m*, 1021*m*, 902*w*, 858*w*, 840*m*, 829*m*, 780*m*, 748*m*, 686*m*. ^{1}H-NMR (280 K): 13.91 (*s*, PhN*H*CO); 11.61 (*s*, $MeOC_6H_4NH$); 7.76 (*d*, *J* = 7.5, 2 arom. H); 7.72 (*d*, *J* = 2.8, 1 arom. H); 7.70 (*d*, *J* = 9.0, 2 arom. H); 7.60 (*d*, *J* = 9.1, 1 arom. H); 7.42 (*t*, *J* = 7.5, 2 arom. H); 7.36 (*dd*, *J* = 9.1, 2.9, 1 arom. H); 7.22 (*tt*, *J* = 7.5, 1.2, 1 arom. H); 6.91 (*d*, *J* = 9.0, 2 arom. H); 3.94, 3.81 (2*s*, 2 MeO). ^{13}C-NMR (280 K): 161.3 (*s*, CO); 158.8 (*s*, C(7)); 156.1 (*s*, 1 arom. C); 151.1 (*s*, C(3)); 139.7 (*s*, C(4a)); 137.4 (*s*, 1 arom. C); 132.9 (*s*, 1 arom. C); 132.6 (*s*, C(8a)); 129.5 (*d*, 2 arom. CH); 128.8 (*d*, C(5)); 126.5 (*d*, C(6)); 125.8, 123.2, 122.0 (3*d*, 5 arom. CH); 121.3 (*s*, C(2)); 114.2 (*d*, 2 arom. CH); 98.0 (*d*, C(8)); 56.5, 55.8 (2*q*, 2 MeO). ESI-MS: 417 ($[M+H]^+$).

7-Methoxy-N-*(4-methoxyphenyl)-3-(phenylamino)quinoxaline-2-carboxamide 1-Oxide* (**6e′**). MPLC: 25.0 mg (5%). Red crystals. M.p. 186–188°. Crystallization from CD_2Cl_2 yielded suitable crystals for an X-ray crystal-structure determination. IR: 3074*m*, 2927*m*, 2834*m*, 1659*m*, 1591*s*, 1541*s*, 1509*s*, 1494*s*, 1464*m*, 1442*m*, 1429*m*, 1392*m*, 1371*m*, 1345*m*, 1328*m*, 1301*m*, 1277*s*, 1262*m*, 1249*s*, 1209*s*, 1169*m*, 1130*m*, 1114*m*, 1090*m*, 1074*m*, 1033*m*, 1022*m*, 930*w*, 894*w*, 829*m*, 779*m*, 752*m*, 703*w*, 689*m*. ^{1}H-NMR (300 K): 13.78 (*s*, $MeOC_6H_4NHCO$); 11.90 (*s*, PhN*H*); 7.85 (*d*, *J* = 7.5, 2 arom. H); 7.76 (*d*, *J* = 2.8, 1 arom. H); 7.75–7.65 (*m*, 3 arom. H); 7.45–7.35 (*m*, 3 arom. H); 7.09 (*tt*, *J* = 7.4, 1.1, 1 arom. H); 6.95 (*d*, *J* = 9.0, 2 arom. H); 3.96, 3.83 (2*s*, 2 MeO). ^{13}C-NMR (300 K): 161.1 (*s*, CO); 159.3 (*s*, C(7)); 157.9 (*s*, 1 arom. C); 151.0 (*s*, C(3)); 140.3 (*s*, 1 arom. C); 139.6 (*s*, C(4a)); 133.0 (*s*, C(8a)); 130.6 (*s*, 1 arom. C); 129.3 (*d*, 2 arom. CH); 129.1 (*d*, C(5)); 126.5 (*d*, C(6)); 123.7, 123.6 (2*d*, 3 arom. CH); 121.9 (*s*, C(2)); 121.4, 114.8 (2*d*, 4 arom. CH); 98.4 (*d*, C(8)); 56.6, 56.0 (2*q*, 2 MeO). ESI-MS: 417 ($[M+H]^+$). Anal. calc. for $C_{23}H_{20}N_4O_4$ (416.44): C 66.34, H 4.84, N 13.45; found: C 66.56, H 4.65, N 13.19.

4. *3-Nitroquinoline-2,4-diamines* **7**. *3-Nitro-*N^4*-(4-Nitrophenyl)-*N^2*-phenylquinoline-2,4-diamine* (**7b**). CC: 43.3 mg (9%). Wine-red crystals. M.p. 185–186°. Crystallization from CD_2Cl_2 yielded suitable crystals for an X-ray crystal-structure determination. IR: 3372*s*, 2924*w*, 2853*w*, 1606*s*, 1583*s*, 1570*s*, 1537*s*, 1509*s*, 1446*m*, 1426*m*, 1336*s*, 1312*s*, 1263*m*, 1250*m*, 1223*m*, 1188*m*, 1144*w*, 1115*m*, 1090*w*, 1074*m*, 928*w*, 900*w*, 867*w*, 846*m*, 821*w*, 798*w*, 756*m*, 690*m*. ^{1}H-NMR (300 K): 9.78 (*s*, $NO_2C_6H_4NH$); 9.49 (*s*, PhN*H*); 8.13 (*d*, *J* = 9.1, 2 arom. H); 7.77 (*d*, *J* = 7.6, 2 arom. H); 7.7–7.6 (*m*, 2 arom. H); 7.52 (*d*, *J* = 8.5, 1 arom. H); 7.40 (*t*, *J* = 7.9, 2 arom. H); 7.16 (*t*, *J* = 7.4, 1 arom. H); 7.1–7.05 (*m*, 3 arom. H). ^{13}C-NMR (300 K): 149.6 (*s*, C(8a)); 148.6 (*s*, 1 arom. C); 147.1 (*s*, C(2)); 146.3 (*s*, C(4)); 143.6, 139.3 (2*s*, 2 arom. C); 134.3 (*d*, C(7)); 129.2 (*d*, 2 arom. CH); 128.3 (*d*, C(8)); 127.0 (*d*, C(5)); 125.8 (*d*, 2 arom. CH); 125.2 (*s*, C(3)); 124.3 (*d*, 1 arom. CH); 123.8 (*d*, C(6)); 122.1, 120.3 (2*d*, 4 arom. CH); 116.5 (*s*, C(4a)). ESI-MS: 424 ($[M+Na]^+$), 402 ($[M+H]^+$). Anal. calc. for $C_{21}H_{15}N_5O_4$ (401.38): C 62.84, H 3.77, N 17.45; found: C 63.06, H 3.83, N 17.71.

*6-Methoxy-3-nitro-*N^2,N^4*-diphenylquinoline-2,4-diamine* (**7c**). MPLC: 9.3 mg (2%). Wine-red crystals. M.p. 139–140°[21]. IR: 3336*w*, 3056*w*, 2956*w*, 2924*m*, 2853*w*, 1579*s*, 1546*s*, 1496*s*, 1473*s*, 1438*m*, 1428*m*, 1398*w*, 1342*w*, 1302*m*, 1276*s*, 1264*m*, 1235*m*, 1168*m*, 1100*w*, 1074*w*, 1031*m*, 982*w*, 914*w*, 897*w*, 843*w*, 831*m*, 781*w*, 766*w*, 751*m*, 703*m*, 689*m*. ^{1}H-NMR (300 K): 10.54, 9.86 (2*s*, 2 PhN*H*); 7.80 (*d*, *J* = 7.5, 2 arom. H); 7.53 (*d*, *J* = 9.1, 1 arom. H); 7.4–7.35 (*m*, 4 arom. H); 7.25–7.2 (*m*, 2 arom. H); 7.17 (*d*, *J* = 8.3, 2 arom. H); 7.13 (*t*, *J* = 7.6, 1 arom. H); 6.82 (*d*, *J* = 2.8, 1 arom. H); 3.33 (*s*, 1 MeO). ^{13}C-NMR (300 K): 154.9 (*s*, C(6)); 148.8 (*s*, C(4)); 146.7 (*s*, C(2)); 145.4 (*s*, C(8a)); 142.5, 140.2 (2*s*, 2 arom. C); 130.2 (*d*, 2 arom. CH); 129.6 (*d*, C(8)); 129.2, 126.1 (2*d*, 3 arom. CH); 126.0 (*d*, C(7)); 123.8 (*d*, 3 arom. CH); 123.0 (*s*, C(3)); 122.0 (*d*, 2 arom. CH); 116.2 (*s*, C(4a)); 106.8 (*d*, C(5)); 55.4 (*q*, MeO). ESI-MS: 387 ($[M+H]^+$).

*6-Methoxy-*N^2*-(4-methoxyphenyl)-3-nitro-*N^4*-phenylquinoline-2,4-diamine* (**7e**). MPLC: 20.0 mg (4%). Dark wine-red crystals. M.p. 181–182°. IR: 3335*w*, 3290 (br.), 3064*w*, 2998*w*, 2926*w*, 2830*w*, 1569*s*, 1548*s*, 1501*s*, 1464*s*, 1438*m*, 1394*m*, 1360*m*, 1322*m*, 1297*m*, 1272*s*, 1243*s*, 1174*m*, 1134*m*, 1115*m*, 1098*m*, 1031*m*, 910*w*, 866*w*, 835*m*, 827*m*, 803*w*, 779*m*, 761*m*, 702*m*, 694*m*. ^{1}H-NMR (290 K): 10.65 (*s*, PhN*H*); 9.78 (*s*, $MeOC_6H_4NH$); 7.66 (*d*, *J* = 8.9, 2 arom. H); 7.45 (*d*, *J* = 9.1, 1 arom. H); 7.38 (*t*, *J* = 8.0, 2 arom. H); 7.22 (*t*, *J* = 7.5, 1 arom. H); 7.2–7.15 (*m*, 3 arom. H); 6.94 (*d*, *J* = 9.0, 2 arom. H); 6.77 (*d*, *J* = 2.8, 1 arom. H); 3.84, 3.30 (2*s*, 2 MeO). ^{13}C-NMR (290 K): 156.5 (*s*, 1 arom. C); 154.5 (*s*, C(6)); 149.0 (*s*, C(4)); 147.2 (*s*, C(2)); 145.6 (*s*, C(8a)); 142.4, 133.0 (2*s*, 2 arom. C); 130.1 (*d*, 2 arom. CH); 129.4 (*d*, C(8)); 126.0 (*d*, C(7)); 126.0 (*d*, 1 arom. CH); 124.1, 123.7 (2*d*, 4 arom. CH); 122.6 (*s*, C(3)); 115.7 (*s*, C(4a)); 114.3 (*d*, 2 arom. CH); 106.6 (*d*, C(5)); 55.9, 55.3 (2*q*, 2 MeO). ESI-MS: 417 ($[M+H]^+$).

*6-Methoxy-*N^4*-(4-methoxyphenyl)-3-nitro-*N^2*-phenylquinoline-2,4-diamine* (**7e′**). MPLC: 25.0 mg (5%). Dark lilac crystals. M.p. 176–177°. IR: 3320*m*, 3011*w*, 2924*m*, 2853*m*, 1610*m*, 1576*s*, 1549*s*, 1498*s*, 1461*s*, 1428*m*, 1393*m*, 1354*m*, 1294*s*, 1249*s*, 1233*s*, 1189*m*, 1170*m*, 1132*s*, 1095*m*, 1027*s*, 898*w*, 879*w*, 835*m*, 776*w*, 754*m*, 708*m*, 689*m*. ^{1}H-NMR (286 K): 10.84 (*s*, $MeOC_6H_4NH$); 10.05 (*s*, PhN*H*); 7.79 (*d*, *J* = 7.6, 2 arom. H); 7.47 (*d*, *J* = 9.1, 1 arom. H); 7.37 (*t*, *J* = 7.9, 2 arom. H); 7.15 (*dd*, *J* = 9.1, 2.8, 1 arom. H); 7.13 (*d*, *J* = 8.6, 2 arom. H); 7.10 (*tt*, *J* = 7.3, 1.1, 1 arom. H); 6.90 (*d*, *J* = 8.6, 2 arom. H); 6.81 (*d*, *J* = 2.8, 1 arom. H); 3.80, 3.31 (2*s*, 2 MeO). ^{13}C-NMR (286 K): 158.1 (*s*, 1 arom. C); 154.4 (*s*, C(6)); 149.8 (*s*, C(4)); 146.8 (*s*, C(2)); 145.1 (*s*, C(8a)); 140.1, 135.1 (2*s*, 2 arom. C); 129.4 (*d*, C(8)); 129.1, 125.7 (2*d*, 4 arom. CH); 125.6 (*d*, C(7)); 123.6, 121.9 (2*d*, 3 arom. CH); 121.7 (*s*, C(3)); 115.7 (*s*, C(4a)); 115.2 (*d*, 2 arom. CH); 106.7 (*d*, C(5)); 56.0, 55.4 (2*q*, 2 MeO). ESI-MS: 417 ($[M+H]^+$).

5. N-*Aryl-4-(arylimino)-5-(4-fluorophenyl)-4,5-dihydro-1,2,5-oxadiazole-3-carboxamides* **8**. *5-(4-Fluorophenyl)-4-[(4-fluorophenyl)imino]-4,5-dihydro-*N*-phenyl-1,2,5-oxadiazole-3-carboxamide* (**8d**). MPLC: 14.1 mg (3%). Yellow crystals. M.p. 133–134° (dec.). Crystallization from CD_2Cl_2/hexane yielded suitable crystals for an X-ray crystal-structure determination. IR: 3025*w*, 2995 (br.), 1702*s*, 1632*s*, 1602*m*, 1567*m*, 1503*s*, 1450*m*, 1396*w*, 1297*w*, 1266*w*, 1230*s*, 1211*m*, 1152*w*, 1094*w*, 1079*w*, 1040*m*, 907*w*, 878*w*, 841*m*, 824*m*, 814*m*, 783*w*, 768*m*, 691*m*. ^{1}H-NMR (280 K): 11.65 (*s*, PhN*H*CO); 7.73 (*d*, *J* = 7.5, 2 arom. H); 7.41 (*t*, *J* = 7.9, 2 arom. H); 7.21 (*tt*, *J* = 7.4, 1.1, 1 arom. H); 7.14 (*dd*, *J* = 9.1, ^4J(H,F) = 4.9, 2 arom. H); 6.99 (*t*, *J* = 9.1, ^3J(H,F) = 8.6, 2 arom. H); 6.85–6.75 (*m*, 4 arom. H). ^{13}C-NMR (280 K): 163.6 (*d*, ^1J(C,F) = 251.8, 1 arom. C); 159.6 (*d*, ^1J(C,F) = 242.9, 1 arom. C); 153.8 (*s*, CO); 147.4 (*s*, C(3)); 145.0 (*s*, C(4)); 141.2, 137.6, 131.1 (3*s*, 3 arom. C); 129.6 (*d*, 2 arom. CH); 128.8 (*dd*, ^3J(C,F) = 9.4, 2 arom. CH); 125.7 (*d*, 1 arom. CH); 123.2 (*dd*, ^3J(C,F) = 8.2, 2 arom. CH); 120.7 (*d*, 2 arom. CH); 116.8 (*dd*, ^2J(C,F) = 23.4, 2 arom. CH); 115.6 (*dd*, ^2J(C,F) = 22.7, 2 arom. CH). ESI-MS: 415 ($[M+Na]^+$). Anal. calc. for $C_{21}H_{14}F_2N_4O_2$ (392.36): C 64.28, H 3.60, N 14.28; found: C 64.05, H 3.76, N 14.07.

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[21]) At *ca.* 127°, a transformation of the crystals was observed.

Table 4. *Crystallographic Data for Compounds* **6a**, **6e**, **6e′**, **7b**, **8d**, *and* **9**

	6a	**6e**	**6e′**	**7b**	**8d**	**9**
Crystallized from	CH_2Cl_2	CD_2Cl_2	CD_2Cl_2	CD_2Cl_2	CD_2Cl_2/hexane	DMSO
Empirical formula	$C_{21}H_{16}N_4O_2$	$C_{23}H_{20}N_4O_4$	$C_{23}H_{20}N_4O_4$	$C_{21}H_{15}N_5O_4$	$C_{21}H_{14}F_2N_4O_2$	$C_{22}H_{18}N_4O_3 \cdot C_2H_6OS$
Formula weight [g mol^{-1}]	356.38	416.43	416.44	401.38	392.36	464.54
Crystal color, habit	red, prism	dark lilac, prism	wine red, prism	red, plate	yellow, prism	yellow, plate
Crystal dimensions [mm]	$0.23 \times 0.30 \times 0.43$	$0.43 \times 0.38 \times 0.25$	$0.20 \times 0.43 \times 0.50$	$0.20 \times 0.45 \times 0.50$	$0.25 \times 0.33 \times 0.45$	$0.06 \times 0.26 \times 0.48$
Temp. [K]	173(1)	173(1)	173(1)	173(1)	173(1)	173(1)
Crystal system	orthorhombic	monoclinic	triclinic	triclinic	monoclinic	monoclinic
Space group	$Pna2_1$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$I2/a$	$P2_1/c$
Z	4	4	2	2	16	4
Reflections for cell determination	25	25	25	25	25	21
2θ Range for cell determination [°]	37–39	36–40	38–40	39–40	37–40	20–39
Unit cell parameters a [Å]	8.074(2)	13.239(2)	10.637(2)	9.958(2)	25.150(4)	11.362(3)
b [Å]	18.697(2)	6.860(2)	11.032(1)	10.008(3)	13.920(2)	9.465(3)
c [Å]	11.011(2)	22.374(2)	10.011(2)	9.841(3)	21.007(4)	21.081(3)
α [°]	90	90	99.38(1)	104.27(2)	90	90
β [°]	90	101.772(8)	114.67(1)	109.23(2)	90.53(1)	90.72(2)
γ [°]	90	90	106.28(1)	90.28(2)	90	90
V [Å]	1662.3(4)	1989.4(6)	970.5(3)	893.5(4)	7354(2)	2266.8(9)
D_x [g cm^{-3}]	1.424	1.390	1.425	1.492	1.417	1.361
$\mu(\mathrm{Mo}K_\alpha)$ [mm^{-1}]	0.0950	0.0975	0.100	0.107	0.108	0.182
$2\theta_{(\max)}$ [°]	55	55	55	55	55	55
Total reflections measured	4475	5150	4699	4315	8970	5801
Symmetry independent reflections	3828	4560	4463	4083	8423	5212
Reflections used [$I > 2\sigma(I)$]	3332	3286	3133	3237	4727	2645
Parameters refined	308	361	361	332	533	299
Final R	0.0386	0.0448	0.0427	0.0409	0.0498	0.0604
wR ($w = [\sigma^2(F_o) + (0.005F_o)^2]^{-1}$)	0.0355	0.0421	0.0381	0.0407	0.0434	0.0495
Goodness of fit	1.699	1.925	1.927	2.127	1.616	1.563
Secondary extinction coefficient	$1.11(5) \times 10^{-6}$	$7.1(6) \times 10^{-7}$	$4.1(8) \times 10^{-7}$	$1.7(2) \times 10^{-6}$	$4.0(3) \times 10^{-8}$	$8(6) \times 10^{-8}$
Final $\Delta_{\max}/\sigma$	0.0002	0.0005	0.0002	0.0003	0.0002	0.0001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.19; −0.20	0.27; −0.24	0.27; −0.19	0.27; −0.23	0.26; −0.29	0.31; −0.36

N,*5-Bis(4-fluorophenyl)-4,5-dihydro-4-(phenylimino)-1,2,5-oxadiazole-3-carboxamide* (**8d′**). MPLC: 14.1 mg (3%). Yellow crystals. M.p. 141–143° (dec.). IR: 2941 (br.), 1705*s*, 1634*s*, 1591*m*, 1558*m*, 1505*s*, 1484*m*, 1414*w*, 1393*w*, 1293*w*, 1228*s*, 1214*m*, 1154*m*, 1096*w*, 1072*w*, 1031*m*, 1013*w*, 998*w*, 992*w*, 905*w*, 862*m*, 837*m*, 785*m*, 765*w*, 731*w*, 698*w*. ^{1}H-NMR (283 K): 11.74 (*s*, FC_6H_4NHCO); 7.72 (*dd*, $J = 9.1$, $^4J(H,F) = 4.9$, 2 arom. H); 7.15–7.05 (*m*, 4 arom. H); 7.04 (*t*, $J = 7.9$, 2 arom. H); 6.92 (*t*, $J = 9.1$, $^3J(H,F) = 8.6$, 2 arom. H); 6.87 (*tt*, $J = 7.4$, 1.1, 1 arom. H); 6.78 (*d*, $J = 7.4$, 2 arom. H). ^{13}C-NMR (283 K): 163.5 (*d*, $^1J(C,F) = 251.8$, 1 arom. C); 160.2 (*d*, $^1J(C,F) = 244.1$, 1 arom. C); 153.9 (*s*, CO); 147.4 (*s*, C(3)); 145.0 (*s*, C(4)); 144.6, 133.9, 131.3 (3*s*, 3 arom. C); 129.0 (*d*, 2 arom. CH); 128.8 (*dd*, $^3J(C,F) = 9.4$, 2 arom. CH); 124.6 (*d*, 1 arom. CH); 122.4 (*dd*, $^3J(C,F) = 8.0$, 2 arom. CH); 121.7 (*d*, 2 arom. CH); 116.7 (*dd*, $^2J(C,F) = 23.5$, 2 arom. CH); 116.2 (*dd*, $^2J(C,F) = 22.6$, 2 arom. CH). ESI-MS: 415 ($[M + Na]^+$). Anal. calc. for $C_{21}H_{14}F_2N_4O_2$ (392.36): C 64.28, H 3.60, N 14.28; found: C 64.00, H 3.76, N 13.97.

6. *3,4-Dihydro-7-methoxy-3-oxo-*N,N′*-diphenylquinoxaline-2-carboximidamide 1-Oxide* (**9**). CC (CH_2Cl_2/MeOH) and recrystallization from CH_2Cl_2/hexane: 120.4 mg (26%). Yellow crystals. M.p. 210–212°. Crystallization from DMSO yielded suitable crystals for an X-ray crystal-structure determination. IR: 3304*m*, 3057*m*, 2860*m*, 1648*s*, 1590*s*, 1531*s*, 1492*s*, 1444*s*, 1384*m*, 1363*s*, 1328*m*, 1274*s*, 1221*s*, 1186*w*, 1145*w*, 1124*m*, 1090*w*, 1076*w*, 1027*m*, 960*w*, 887*w*, 827*w*, 789*m*, 759*m*, 698*m*. ^{1}H-NMR ((D$_6$)acetone, 220 K): 11.74 (*s*, N*H*CO); 9.06 (*s*, PhN*H*); 7.90 (*d*, $J = 7.6$, 2 arom. H); 7.57 (*d*, $J = 2.1$, 1 arom. H); 7.40 (*d*, $J = 8.9$, 1 arom. H); 7.33 (*t*, $J = 7.4$, 2 arom. H); 7.26 (*d*, $J = 8.9$, 1 arom. H); 7.10 (*t*, $J = 7.5$, 2 arom. H); 7.02 (*t*, $J = 7.1$, 1 arom. H); 6.94 (*d*, $J = 7.6$, 2 arom. H); 6.87 (*t*, $J = 7.1$, 1 arom. H); 3.89 (*s*, MeO). ^{13}C-NMR ((D$_6$)acetone, 220 K): 156.8 (*s*, C(7)); 155.0 (*s*, CO); 150.3 (*s*, 1 arom. C); 144.8 (*s*, CN(NH)); 141.6 (*s*, 1 arom. C); 136.7 (*s*, C(2)); 130.7 (*s*, C(8a)); 129.5, 129.1 (2*d*, 4 arom. CH); 127.0 (*s*, C(4a)); 124.0 (*d*, C(6)); 123.7, 123.0, 120.8, 118.5 (4*d*, 6 arom. CH); 118.5 (*d*, C(5)); 100.6 (*d*, C(8)); 56.0 (*q*, MeO). ESI-MS: 409 ($[M + Na]^+$), 387 ($[M + H]^+$).

7. *Crystal-Structure Determination of* **6a**, **6e**, **6e′**, **7b**, **8d** *and* **9**[22]. All measurements were made on a *Rigaku-AFC5R* diffractometer using graphite-monochromated MoK_α radiation (λ 0.71069 Å) and a 12-kW rotating anode generator. The $\omega/2\theta$ scan mode was employed for data collection. The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. Data collection and refinement parameters are given in *Table 4*, views of the molecules are shown in *Figs. 1–5*. Each structure was solved by direct methods using SHELXS86 [43], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. All of the H-atoms of **6a**, **6e**, **6e′**, and **7b**, as well as the amide H-atom of **8d**, were located in difference electron density maps, and their positions were allowed to refine together with individual isotropic displacement parameters. All of the H-atoms of **9** and the H-atoms bonded to C in **8d** were fixed in geometrically calculated positions (d(C–H) = 0.95 Å), and they were assigned fixed isotropic displacement parameters with a value equal to 1.2 U_{eq} of the parent atom. In the case of **8d**, there are two symmetry-independent molecules in the asymmetric unit. The atomic coordinates of the two molecules were tested carefully for a relationship from a higher symmetry space group using the MISSYM routine [44] of the program PLATON [45], but none could be found. The asymmetric unit of **9** contains one molecule of **9** and one DMSO molecule. Refinement of each structure was carried out on F using full-matrix least-squares procedures, which minimized the function $\sum w(|F_o| - |F_c|)^2$. A correction for secondary extinction was applied in each case. Neutral-atom scattering factors for non-H-atoms were taken from [46a] and the scattering factors for H-atoms from [47]. Anomalous dispersion effects were included in F_{calc} [48]; the values for f' and f'' were those of [46b]. All calculations were performed using the TEXSAN crystallographic software package [49].

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[22] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-111717–111722 for **6a**, **6e**, **6e′**, **7b**, **8d**, and **9**, respectively. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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