Synthesis, Structure and Mass Spectral Fragmentation of a Series of Substituted Furazano[3,4-*b*]quinoxaline 1-Oxides and their Deoxides

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A series of substituted furazano[3,4-*b*]quinoxaline 1-oxides have been prepared by oxidation of the respective 2,3-bis(hydroxyimino)-1,2,3,4-tetrahydroquinoxalines with nitric acid and their structure was confirmed by means of their nmr spectra. A very rapid equilibrium occurs between their two isomeric *N*-oxide forms *via* the dinitroso equivalent, and the influence of the 6(7)-substituents on the equilibrium is discussed. These compounds were easily deoxygenated by triphenylphosphine in quantitative yields to the corresponding furazans. The electron impact mass spectra of both of the above series of compounds have also been recorded and their fragmentation pattern is discussed.

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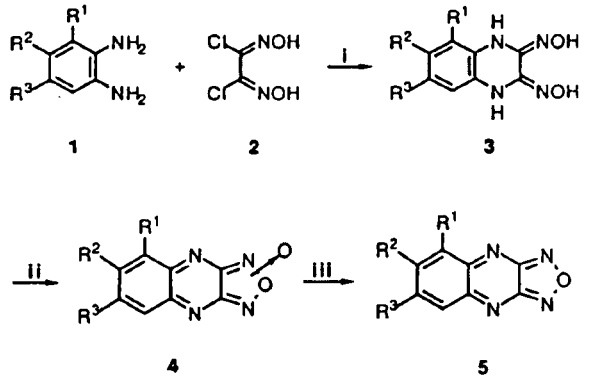
Furazan *N*-oxides and their fused derivatives [1] are excellent precursors for the synthesis of a large number of heterocyclic compounds. In addition, they have attracted considerable pharmacochemical interest [1,2]. Their spectral and chemical properties strongly depend on the presence of the *N*-oxide group and the mobile equilibrium between their two isomeric forms, which has long been postulated to proceed *via* the corresponding 1,2-dinitroso form [1]. 1,2-Dinitrosobenzene was recently [3] isolated and characterized at 12-14 K in argon matrices.

Readily available furazano[3,4-*b*]quinoxaline 1-oxides indicate a remarkable chemical reactivity, which substantially differs from that of benzofurazan *N*-oxides [4]. We have recently shown, both chemically [5] and electrochemically [6], the existence of their 2,3-dinitrosoquinoxaline equivalents as intermediates of their interconversion in solution. However, their real structure in solution is still uncertain, namely the equilibrium between the two *N*-oxide forms has not been studied, its thermodynamic and kinetic parameters have not been determined and the influence of substituents on this equilibrium has not been explored.

Scheme 1



1,3,4,5

a. $R^1 = R^2 = R^3 = H$ d. $R^1 = R^3 = H$; $R^2 = Cl$ g. $R^1 = H$; $R^2 = R^3 = MeO$

b. $R^1 = Me$; $R^2 = R^3 = H$ e. $R^1 = R^3 = H$; $R^2 = MeO$ h. $R^1 = H$; $R^2 = R^3 = Cl$

c. $R^1 = R^3 = H$; $R^2 = Me$ f. $R^1 = H$; $R^2 = R^3 = Me$

Reagents and Conditions:

(i) aqueous Na_2CO_3 2N, CH_2Cl_2, 0-5°C.

(ii) Conc. HNO_3, CH_2Cl_2, r.t., 20-51% (from 1 to 4).

(iii) Ph_3P, CH_2Cl_2, r.t., 79-99%.

Synthesis and Structure of Furazano[3,4-*b*]quinoxaline 1-Oxides.

Mono- and bis-substituted derivatives of the title compounds **4a-h** (Scheme 1) have been prepared by slight modification of the literature procedures [4], *e.g.* using nitric acid as the oxidant instead of iodosobenzene bis(trifluoroacetate) or lead(IV) acetate and without characterizing the intermediate 2,3-bis(hydroxyimino)-1,2,3,4-tetrahydroquinoxalines **3**. Compounds **4a-h** were easily deoxygenated by triphenylphosphine in quantitative yields to give the corresponding deoxides **5a-h**.

The ^1H and ^{13}C nmr spectra of compounds **4a-h** and **5a-h** obtained at 20° in saturated deuteriochloroform solutions are recorded in Tables 1 and 2. The systematic numbering is used in all the cases. For reasons of convenience, the numbering adopted for the monosubstituted compounds **4b-e** in Tables 1 and 2 is that of the 5- or 6-substituted furazano[3,4-*b*]quinoxaline 1-oxides, although they exist in equilibrium with the corresponding 8- or 7-substituted isomers .

The fact that both isomers **4A** and **4B** (Scheme 2) of the unsymmetrically substituted compounds **4b-e** exist in solution and the recorded spectra are the average ones of the two species and not those of one isomer, could be concluded by analogy to the spectra of the symmetrically substituted compounds **4a,f-h**, that are the average spectra between **4A** and **4B**. It is, also, most unlikely that only one of the two isomeric *N*-oxides of compounds **4b-e** is

Table 1

^{1}H-NMR Spectra of Compounds **4a-h** and **5a-h**, δ ($CDCl_3$) (J, Hz)

Compound	5-H	6-H	7-H	8-H	Me
4a [a]	7.89 m	7.71 m	7.71 m	7.89 m	-
4b [b]	-	7.53 ddq (6.5,1.4,1.4)	7.62 dd (9.1,6.5)	6.69 d (9.1)	2.70 s
4c [c]	7.60 s	-	7.55 dd (9.2,1.6)	7.77 d (9.2)	2.57 s
4d	6.98 d (2.6)	-	7.39 dd (9.8,2.6)	7.73 d (9.8)	4.04 s
4e	7.90 d (2.3)	-	7.65 dd (9.8,2.2)	7.86 d (9.8)	-
4f	7.59 s	-	-	7.59 s	2.49 s
4g	6.96 s	-	-	6.96 s	4.09 s
4h	8.06 s	-	-	8.06 s	-
5a [a]	7.99 m	7.81 m	7.81 m	7.99 m	-
5b [b]	-	7.59 ddq (4.4,1.3,1.3)	7.69 dd (9.2,4.4)	6.79 d (9.2)	2.76 s
5c	7.71 ddq (2.0,1.0,0.5)	-	7.61 dd (9.4,2.0)	7.87 dd (9.4,0.5)	2.61 d (1.0)
5d	7.05 d (2.6)	-	7.46 dd (10.0,2.6)	7.83d (10.0)	4.08 s
5e	8.00 dd (2.2,0.5)	-	7.75 dd (9.3,2.2)	7.98 dd (9.3,0.5)	-
5f	7.69 q (1.0)	-	-	7.69 q (1.0)	2.49 d (1.0)
5g	7.05 s	-	-	7.05 s	4.11 s
5h	8.16 s	-	-	8.16 s	-

[a] AA'BB' system. [b] Broadened signals for 5-Me and 8-H, due to small coupling of 5-Me with 6-H, 5-Me with 8-H, and 6-H with 8-H. [c] Similarly, 5-H and 6-Me broadened singlets.

Table 2

^{13}C-NMR Assignments of Compounds **4a-h** and **5a-h**, δ ($CDCl_3$)

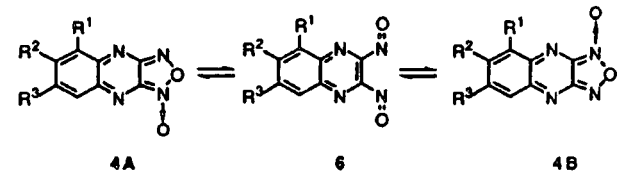
Compound	C-3a/C-9a	C-4a/C-8a	C-5	C-6	C-7	C-8	Me
4a	[a]	149.4	130.4	134.9	134.9	130.4	-
4b	[a]	149.5/149.8	139.0	133.4	135.2	128.2	17.6
4c	118.0/137.9	148.7/149.6	127.7	146.8	138.4	129.7	22.6
4d	[a]	147.8/151.5	103.5	164.7	132.5	131.3	56.7
4e	[a]	147.8/148.9	128.1	142.1	136.6	131.3	-
4f	[a]	149.2	128.0	147.8	147.8	128.0	20.9
4g	[a]	148.3	104.5	158.5	158.5	104.5	57.1
4h	[a]	147.4	129.7	141.2	141.2	129.7	-
5a	151.7	150.9	130.7	135.0	135.0	130.7	-
5b	151.2/151.4	150.8/151.2	139.2	133.3	135.4	128.5	17.8
5c	151.7/151.8	150.2/150.9	127.9	146.8	138.6	130.1	22.6
5d	151.3/151.7	149.5/152.4	103.4	164.6	133.0	131.7	56.7
5e	151.5/151.6	149.3/150.1	128.4	142.3	136.8	131.7	-
5f	151.8	150.5	128.2	147.9	147.9	128.2	21.0
5g	151.4	150.6	104.5	158.7	158.7	104.5	57.2
5h	151.6	148.8	130.0	141.5	141.5	130.0	-

[a] Signals did not appear.

formed by oxidation of the corresponding oximes, since only one product was isolated from this reaction in all cases.

The equilibrium between the two isomeric forms **4A** and **4B** of compounds **4a-h** (Scheme 2) is very fast and

Scheme 2



4A **6** **4B**

the coalescence point much lower than 20° in both ^{1}H and ^{13}C nmr spectra. Unfortunately, with the exception of **4c**, the C-3a, C-9a signals did not appear, owing to the low concentration due to insolubility of these compounds and the long relaxation times of these carbons rather than to broadening of the peaks because of their coalescence. Attempted variable temperature nmr investigation of this equilibrium failed, because of solubility problems. The ^{13}C nmr spectrum of **4c** remained unchanged at -30° and the ^{1}H nmr spectrum of **4f** at -55° was identical to that at 20°.

The large difference between the C-3a and C-9a chemical shifts in the 6(7)-methylfurazano[3,4-*b*]quinoxaline 1-oxide **4c** (*ca.* Δδ = 20), which are strongly affected by the presence of the *N*-oxide group [7], is evidently due to the fact that one of the two isomers **4cA** or **4cB** is favored. It has been reported [1c], that substitution at the 5(6)-position in benzofurazan *N*-oxide changes the equilibrium constant between the two *N*-oxide isomers; usually, the 6-

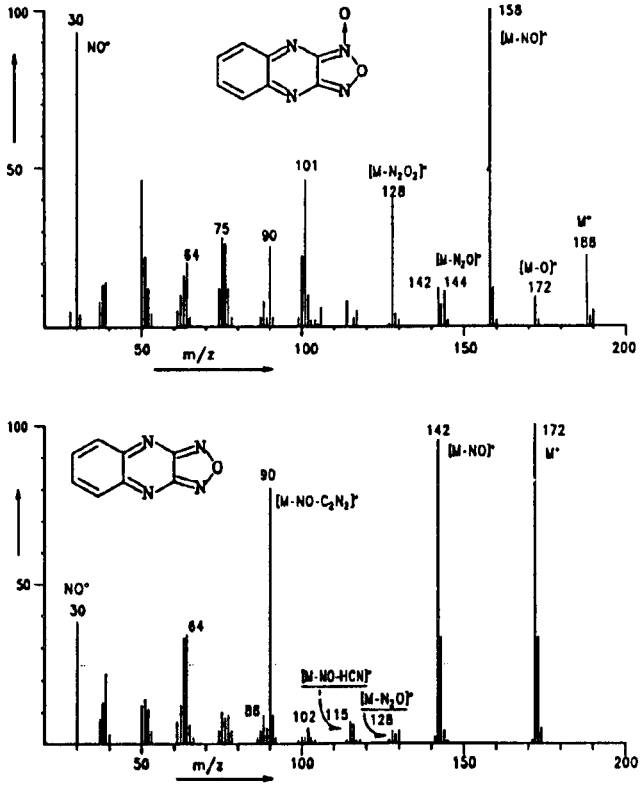


Figure 1. Mass spectra of compounds 4a and 5a.

Table 3

Chemical Shift Diferences ($\Delta\delta = \delta_{FZ}-\delta_{FX}$) between the Respective Carbons of Compounds **4** (δ_{FX}) and **5** (δ_{FZ})

Entry	C-5	C-6	C-7	C-8
a	+0.3	+0.1	+0.1	+0.3
b	+0.2	-0.1	+0.2	+0.3
c	+0.2	+0.0	+0.2	+0.4
d	-0.1	-0.1	+0.5	+0.4
e	+0.3	+0.2	+0.2	+0.4
f	+0.2	+0.1	+0.1	+0.2
g	+0.0	+0.2	+0.1	+0.0
h	+0.3	+0.3	+0.3	+0.3

isomer is favored when the substituent is an electron-acceptor group, while the electron-releasing substituents lead to preference for the 5-isomer, but there is no clear correlation with their electron-donor properties [1c]. In the case of 6(7)-methylfurazano[3,4-*b*]quinoxaline 1-oxide **4c**, the substituent changes the two equilibrium constants, favoring one of the two isomers **4A** or **4B** and subsequently affects the shielding of the C-3a/C-9a carbons. Unfortunately, the highly diagnostic C-3a/C-9a signals did not appear for the rest of the compounds **4**.

The failure to obtain spectra below the coalescence temperature does not allow any direct diagnosis about the

Table 4

Main Fragments in the 70 eV EI Mass Spectra of Compounds **4**, m/z (Relative Intensities)

Fragment	**4a**	**4b**	**4c**	**4d**	**4e**	**4f**	**4g**	**4h**
[M+1]	189	203	203	219	223/225	217	249	257/259
	(2)	(6)	(4)	(13)	(4)	(4)	(23)	(1)
[M]	188	202	202	218	222/224	216	248	256/258
	(22)	(27)	(21)	(13)	(22)	(15)	(32)	(22)
[M-O]	172	186	186	202	206/208	200	232	240/242
	(10)	(17)	(11)	(11)	(7)	(7)	(41)	(9)
[M-NO]	158	172	172	188	192/194	186	218	226/228
	(100)	(100)	(100)	(100)	(100)	(87)	(96)	(100)
[M-N_2O]	144	158	158	174	178/180	172	204	212/214
	(11)	(9)	(11)	(10)	(15)	(16)	(22)	(28)
[M-O-NO]	142	156	156	172	176/178	170	202	210/212
	(12)	(13)	(22)	(25)	(15)	(19)	(68)	(20)
[M-N_2O_2]	128	142	142	158	162/164	156	188	196/198
	(40)	(46)	(71)	(87)	(49)	(94)	(100)	(51)
[M-NO-NOH]	127	141	141	157	161/163	155	187	195/197
	(0.5)	(28)	(41)	(7)	–	(35)	(4)	–
[M-N_2O-HCN]	117	131	131	147	151/153	145	177	185/187
	(5)	(12)	(5)	(3)	(2)	(4)	(15)	(4)
[M-O-NO-CN]	116	130	130	146	150/152	144	176	184/186
	(5)	(3)	(2)	(1)	(1)	(0.5)	(1)	–
[M-O-NO-HCN]	115	129	129	145	149/151	143	175	183/185
	(2)	(12)	(7)	(3)	(0.5)	(4)	(7)	–
[M-NO-C_2N_2]	106	120	120	136	140/142	134	166	174/176
	(6)	(9)	(10)	(1)	(4)	(14)	(16)	(9)
[M-N_2O_2-CN]	102	116	116	132	136/138	130	162	170/172
	(10)	(18)	(20)	(0.5)	(2)	(6)	(2)	(0.5)
[M-N_2O_2-HCN]	101	115	115	131	135/137	129	161	169/171
	(46)	(82)	(71)	(5)	(7)	(16)	(2)	(0.5)
[M-NO-NOH-HCN]	100	114	114	130	134/136	128	160	168/170
	(22)	(43)	(34)	(7)	-	(17)	(9)	–
[M-O-NO-C_2N_2]	90	104	104	120	124/126	118	150	158/160
	(25)	(6)	(13)	(6)	(20)	(6)	(28)	(23)
[M-O-NO-CN-HCN]	89	103	103	119	123/125	117	149	157/159
	(4)	(6)	(4)	(0.5)	–	(4)	(0.5)	–
[M-O-NO-2HCN]	88	102	102	118	122/124	116	148	156/158
	(8)	(11)	(7)	(0.5)	–	(13)	(1)	–
[M-N_2O_2-C_2N_2]	76	90	90	106	110/112	104	136	144/146
	(26)	(8)	(6)	(1)	(4)	(3)	(1)	–
[M-N_2O_2-HCN-CN]	75	89	89	105	109/111	103	135	143/145
	(27)	(18)	(15)	(1)	(1)	(8)	(8)	–
[M-N_2O_2-2HCN]	74	88	88	104	108/110	102	134	142/144
	(12)	(20)	(15)	(4)	–	(14)	(1)	–
[M-NO_2-C_2N_2-CN]	64	78	78	94	98/100	92	124	132/134
	(20)	(3)	(5)	-	(4)	(0.5)	-	-
[M-NO_2-C_2N_2-HCN]	63	77	77	93	97/99	91	123	131/133
	(15)	(13)	(17)	(1)	(3)	(5)	–	–

Table 5

Main Fragments in the 70 eV EI Mass Spectra of Compounds 5, m/z (Relative Intensities)

Fragment	5a	5b	5c	5d	5e	5f	5g	5h
[M]	172	186	186	202	206/208	200	232	240/242
	(100)	(58)	(35)	(65)	(63)	(52)	(70)	(42)
[M-NO]	142	156	156	172	176/178	170	202	210/212
	(95)	(87)	(100)	(100)	(100)	(100)	(100)	(100)
[M-N_2O]	128	142	142	158	162/164	156	188	196/198
	(3)	–	–	(2)	(1)	–	(1)	–
[M-NO-CN]	116	130	130	146	150/152	144	176	184/186
	(6)	(4)	(2)	–	(4)	(1)	–	(0.5)
[M-NO-HCN]	115	129	129	145	149/151	143	175	183/185
	(7)	(89)	(20)	(1)	(4)	(7)	–	(1)
[M-N_2O-CN]	102	116	116	132	136/138	130	162	170/172
	(5)	–	(2)	(1)	(1)	(2)	(0.5)	–
[M-N_2O-HCN]	101	115	115	131	135/137	129	161	169/171
	(1)	–	(0.5)	(20)	–	(4)	–	–
[M-NO-C_2N_2]	90	104	104	120	124/126	118	150	158/160
	(80)	(18)	(35)	(11)	(68)	(22)	(38)	(65)
[M-NO-CN-HCN]	89	103	103	119	123/125	117	149	157/159
	(6)	(15)	(5)	(4)	–	(12)	–	–
[M-NO-2HCN]	88	102	102	118	122/124	116	148	156/158
	(9)	(81)	(14)	(3)	–	(47)	–	–
[M-N_2O-2HCN]	74	88	88	104	108/110	102	134	142/144
	(4)	(8)	(3)	(2)	–	(12)	–	–
[M-C_2N_2-CN]	64	78	78	94	98/100	92	124	132/134
	(34)	(14)	(5)	–	(8)	(2)	–	(2)
[M-C_2N_2-HCN]	63	77	77	93	97/99	91	123	131/133
	(33)	(89)	(31)	(2)	(8)	(40)	–	–

favored isomer **4A** or **4B** (Scheme 2) in the discussed compounds. However, some reasonable inferences could be made considering the changes in the quinoxaline C-5, C-6, C-7, C-8 carbon chemical shifts between the *N*-oxides **4** and their deoxide counterparts **5**. As reported in the literature [7], for benzofurazan *N*-oxide, the carbons of the half conjugative system bearing the *N*-oxide group are shielded (δC-6, 128.0; δC-7, 112.1; δC-7a, 113.7), while C-3a (δ 152.2), C-4 (δ 117.3), and C-5 (δ 132.3) are deshielded, in comparison to benzofurazan (δC-3a, 148.6; δC-4, 115.8; δC-5, 131.2). Similarly, in furazano[3,4-*b*]-quinoxaline 1-oxides **4**, it is expected that C-7, C-8, C-8a, C-9a, being in the half conjugative system bearing the *N*-oxide group, will be shielded and C-3a, C-4a, C-5, C-6 will be analogously deshielded.

The symmetrically substituted compounds **4a,f-h** give two peaks for the pairs C-5/C-8 and C-6/C-7. Thus the carbons of each pair suffer the same shielding effect by the *N*-oxide group in respect to their deoxy counterparts **5**, which is expected assuming a rapid equilibrium between **4A**, **4B**, *via* **6** (Scheme 2) is taking place. In the 6(7)-monosubstituted compounds **4c-e**, however, the carbons of the above pairs are not equally shielded by the *N*-oxide group in respect to their deoxide counterparts **5** (Table 3). Thus, in comparison to **5d**, C-7 and C-8 of **4d** (using the given arbitrary numbering in Tables 1 and 2) are shielded (*ca.* 0.5 ppm) by the *N*-oxide group, while C-5, C-6 are slightly deshielded. This difference, although small, indicates that the 6-isomer **4dA** should be predominate over **4dB** in their equilibrium. Similarly, in compounds **4c** and **4e**, the 6-isomers **4A** should be favored in respect to their 7-isomers **4B**, but with a decreased preference of **4A** over **4B** however, since here all carbons are shielded, as in the symmetrically substituted compounds **4a,f-h**, but to a lesser degree for C-5/C-6. For the same reasons, the 5-isomer for **4b** is most likely favored over its 8-isomer.

Mass Spectra of Compounds **4a-h** and **5a-h**.

Furazan *N*-oxides and their fused derivatives give highly diagnostic mass spectra [1a,1c], their most characteristic feature being the loss of oxygen, which has been shown in a recent comprehensive study [8] to be an electron impact ionization process rather than a thermal degradation one.

The electron impact mass spectra of compounds **4a-h** and **5a-h** obtained at 70 eV are presented in Table 4, while representative mass spectra of the parent compounds **4a** and **5a** are shown in Figure 1. They are characterized by the appearance of peaks corresponding to ions generated by successive extrusions of the NO·, CN· and/or HCN fragments.

Inspection in Figure 1 and Table 4 reveals that there are many similarities between the spectra of compounds **4** and **5**. The spectra of furoxans **4** include almost all the peaks of the spectra of their deoxy counterparts **5**, although with differences in their relative intensities. This implies that the $[M-O]^{+\cdot}$ ion of compounds **4**, which is a common fragment in the mass spectra of furoxans [1a,1c,8,9], and the molecular ion $M^{+\cdot}$ of compounds **5**, most probably adopt similar structures in the fragmentation chamber of the spectrometer. A mechanistic scheme for the main fragmentations of compounds **4** is proposed in Scheme 3, whereas Scheme 4 gives the proposed fragmentation paths for compounds **5**.

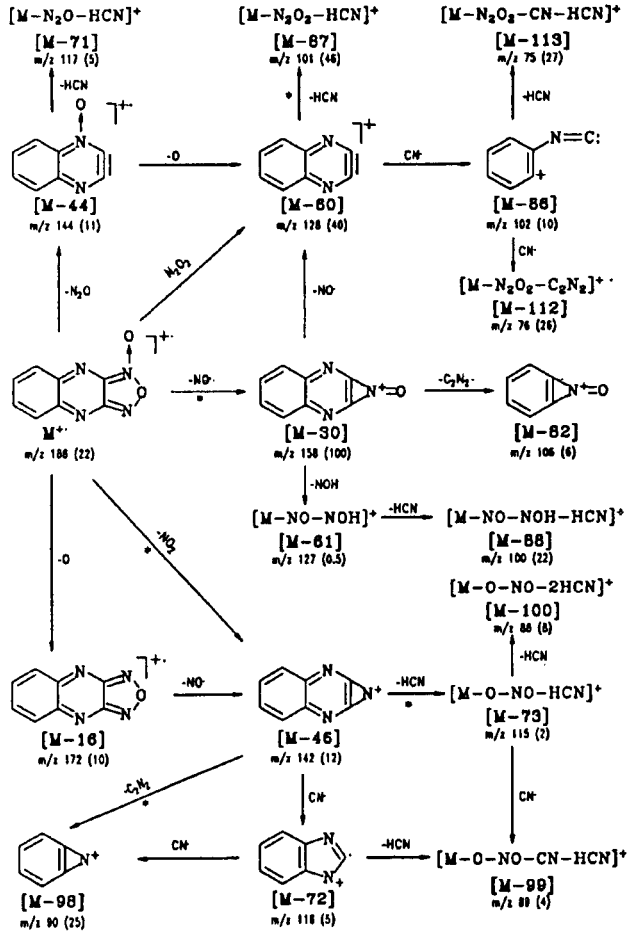
The molecular ion $M^{+\cdot}$ of compounds **4**, which always appears with moderate abundance, is split following mainly three pathways (Scheme 3). Thus, in addition to the $[M-O]^{+\cdot}$ peak, which is generated by an oxygen loss, it further gives the $[M-30]^{+}$ and $[M-44]^{+\cdot}$ ions, by elimination of a NO· or a N_2O fragment respectively. Further elimination of another NO· fragment gives the $[M-N_2O_2]$ ion, for which a benzyne structure has been suggested [8,9]. It is worth mentioning that the $[M-N_2O]^{+\cdot}$ ion has been observed for the first time in furoxan derivatives, and for its formation an oxygen shift in the molecular ion should most probably take place. A similar rearrangement is also required for the formation of the low abundances $[M-82]^{+}$ ion, that is formed from the $[M-NO]^{+}$ by a C_2N_2 elimination and this fragmentation is supported by observed metastable peaks. A C_2N_2 extrusion also occurs in the [M-46] ion, which is formed by a NO· loss of the [M-O] ion, thus giving the [M-98] ion.

Of interest are also the $[M-61]^{+}$ and $[M-88]^{+}$ ions, which can be formed from the $[M-NO]^{+}$ ion by successive NOH and HCN eliminations. These peaks are not present in the spectra of the chloro derivatives **4d,h**, while in the methyl derivatives **4b,c,f** they appear with higher intensities, indicating that the hydrogen of the NOH and HCN fragments is provided mainly by the methyl groups of these compounds. The same behavior has been observed in all the cases where a HCN loss is taking place both in compounds **4** and **5**, where in the case of methyl derivatives, the corresponding peaks are always of higher intensity.

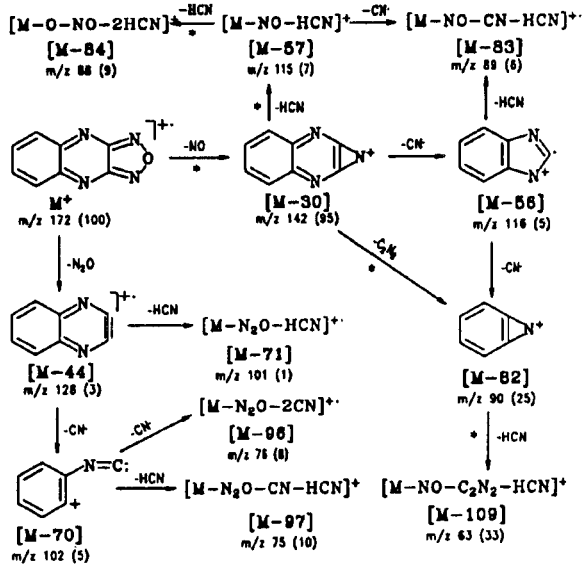
The mass spectra of compounds **4** do not give any possibility for differentiation between the two possible isomers in the asymmetrically substituted derivatives, *i.e.* compounds **4b-e**, since the molecular ion may be found in equilibrium with its open dinitroso structure [1c].

The fragmentation of compounds **5** (Scheme 4) is similar to that of the $[M-O]^{+\cdot}$ ion of compounds **4** and all the peaks of their mass spectra are found also in the spectra

Scheme 3
Main fragmentation pathway of compound **4a**



Scheme 4
Main fragmentation pathway of compound **5a**



of compounds **4** (see Figure 1 and Tables 4 and 5). Their molecular ion $M^{+\cdot}$ appears in high abundance, whereas the $[M-NO]^+$ ion in most cases constitutes the base peak of the spectrum. Of high relative intensity is also the [M-82]+ peak, corresponding to an ion formed by a C_2N_2 elimination from the $[M-O]^+$ ion and this fragmentation is supported by observed metastable peaks.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage microscope and are uncorrected. Microanalyses were performed on a Perkin-Elmer 240B element analyser, while mass spectra were obtained on a Hitachi-Perkin-Elmer MU-6L or on a VG-TS 250 spectrometers at 70 eV. The ^1H nmr spectra were recorded either at 200 MHz on a Varian XL-200 spectrometer or at 300 MHz on a Varian VXR-300 spectrometer and are quoted relative to tetramethylsilane as the internal reference, in deuteriochloroform solutions. The ^{13}C nmr spectra were obtained at 50 or 75 MHz in the same spectrometers in saturated deuteriochloroform solutions and are referred to internal TMS. The ir spectra were recorded on a Perkin-Elmer 1310 spectrometer.

General Procedure for the Synthesis of Furazano[3,4-*b*]quinoxaline 1-Oxides **4a-h**.

To a cold, stirred suspension of 1,2-phenylenediamine **1** (10 mmoles) and 1,2-dichloroglyoxime [10] (1.6g, 10.2 mmoles) in methylene chloride (50 ml), a solution of aqueous 2*N* sodium carbonate (40 ml) was added dropwise, during a period of 30 minutes, while the temperature was kept at 0-5°. The precipitated solid was then collected with filtration, washed thoroughly with methylene chloride and water, and dried in the air. To a stirred suspension of the above solid in methylene chloride (50 ml), concentrated nitric acid 65% (2 ml) was added at room temperature and the solution became immediately colored deep red. After staying 10 minutes at room temperature, the solvent was evaporated off and the residue chromatographed on silica gel using methylene chloride as the eluant to give the desired deep red furazano[3,4-*b*]quinoxaline 1-oxides **4a-h**.

Furazano[3,4-*b*]quinoxaline 1-Oxide **4a**.

This compound was prepared in 30% yield, mp 160-162° (lit [4a] mp 161-162°).

5(8)-Methylfurazano[3,4-*b*]quinoxaline 1-Oxide **4b**.

This compound was prepared in 51% yield, mp 127-129° (lit [4a] mp 128-129°).

6(7)-Methylfurazano[3,4-*b*]quinoxaline 1-Oxide **4c**.

This compound was prepared in 36% yield, mp 150-152° (from chloroform); ir (Nujol): 1580 cm^{-1}.

Anal. Calcd. for $C_9H_6N_4O_2$: C, 53.46; H, 2.99; N, 27.71. Found: C, 53.41; H, 2.78; N, 27.75.

6(7)-Methoxyfurazano[3,4-*b*]quinoxaline 1-Oxide **4d**.

This compound was prepared in 23% yield, mp 166-168° (from chloroform); ir (Nujol): 1590 cm^{-1}.

Anal. Calcd. for $C_9H_6N_4O_3$: C, 49.54; H, 2.77; N, 25.68. Found: C, 49.68; H, 2.88; N, 25.80.

6(7)-Chlorofurazano[3,4-*b*] quinoxaline 1-Oxide **4e**.

This compound was prepared in 39% yield, mp 138-140° (lit [4c] mp 138-140°).

6,7-Dimethylfurazano[3,4-*b*]quinoxaline 1-Oxide **4f**.

This compound was prepared in 40% yield, mp 185-186° (lit [4b] mp 185-186°).

6,7-Dimethoxyfurazano[3, 4-*b*]quinoxaline 1-Oxide **4g**.

This compound was prepared in 20% yield, mp 236-239° (from chloroform); ir (Nujol): 1590 cm^{-1}.

Anal. Calcd. for $C_{10}H_8N_4O_4$: C, 48.39; H, 3.25; N, 22.57. Found: C, 48.34; H, 3.28; N, 22.46.

6,7-Dichlorofurazano[3,4-*b*]quinoxaline 1-Oxide **4h**.

This compound was prepared in 27% yield, mp 195-197° (from chloroform); ir (Nujol): 1570 cm^{-1}.

Anal. Calcd. for $C_8H_2Cl_2N_4O_2$: C, 37.35; H, 0.78; N, 21.78. Found: C, 37.24; H, 0.73; N, 21.67.

General Procedure for the Synthesis of Furazano[3,4-*b*]quinoxalines **5a-h**.

To a solution of **4** (1 mmole) in methylene chloride (10 ml), a solution of triphenylphosphine (262 mg, 1 mmole) in methylene chloride (10 ml) was added and the color immediately turned from deep red to yellow-orange. The solvent was then evaporated off and the mixture was chromatographed on silica gel with methylene chloride as the eluant, to give at first the yellow-orange furazano[3,4-*b*]quinoxalines **5a-h** and afterwards triphenylphosphine oxide.

Furazano[3,4-*b*]quinoxaline **5a**.

This compound was prepared in 87% yield, mp 180-182° (lit [4a] mp 181-182°).

5-Methylfurazano[3,4-*b*]quinoxaline **5b**.

This compound was prepared in 79% yield, mp 137-139° (lit [4a] mp 138-139°).

6-Methylfurazano[3,4-*b*]quinoxaline **5c**.

This compound was prepared in 97% yield, mp 160-163° (from chloroform).

Anal. Calcd. for $C_9H_6N_4O$: C, 58.06; H, 3.25; N, 30.09. Found: C, 58.18; H, 3.29; N, 30.04.

6-Methoxyfurazano[3,4-*b*]quinoxaline **5d**.

This compound was prepared in 99% yield, mp 170-172° (from chloroform).

Anal. Calcd. for $C_9H_6N_4O_2$: C, 53.46; H, 2.99; N, 27.72. Found: C, 53.69; H, 2.84; N, 27.88.

6-Chlorofurazano[3,4-*b*]quinoxaline **5e**.

This compound was prepared in 95% yield, mp 151-153° (lit [4c] mp 151-153°).

6,7-Dimethylfurazano[3,4-*b*]quinoxaline **5f**.

This compound was prepared in 82% yield, mp 215-217° (lit [4b] mp 215-217°).

6,7-Dimethoxyfurazano[3,4-*b*]quinoxaline **5g**.

This compound was prepared in 98% yield, mp 275-278° (from chloroform).

Anal. Calcd. for $C_{10}H_8N_4O_3$: C, 51.72; H, 3.47; N, 24.13. Found: C, 51.88; H, 3.63; N, 24.33.

6,7-Dichlorofurazano[3,4-*b*]quinoxaline **5h**.

This compound was prepared in 95% yield, mp 206-207° (from chloroform).

Anal. Calcd. for $C_8H_2Cl_2N_4O$: C, 39.86; H, 0.84; N, 23.24. Found: C, 39.60; H, 0.91; N, 23.08.

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