J. prakt. Chem. 338 (1996) 414–419

Journal für praktische Chemie
Chemiker-Zeitung

On the Nitrosation of *N*-Monosubstituted 1-Naphthylamines – Formation of *N*-Monosubstituted 4-Nitroso-1-naphthylamine Derivatives and Benzocondensed Indaminium Salts [1])

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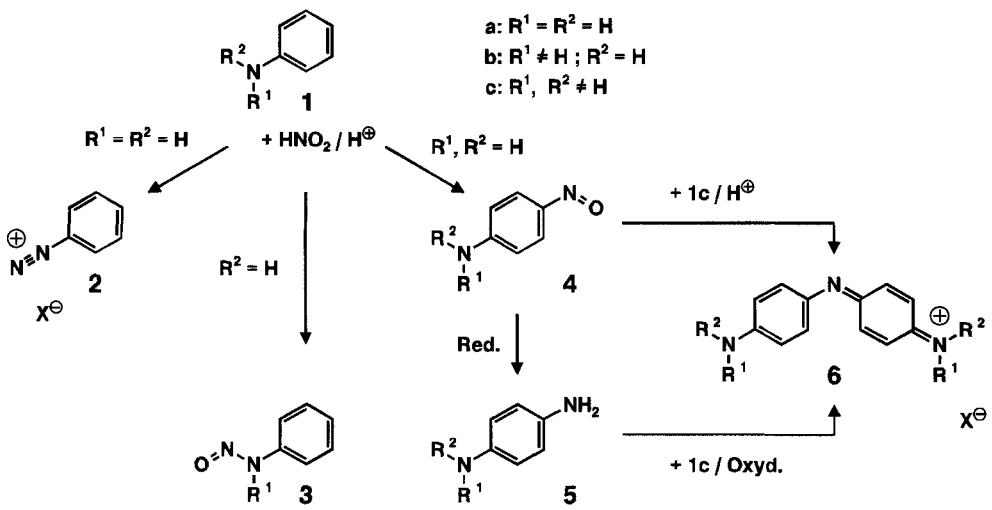
Received March 6th 1996

Dedicated to Prof. Dr. R. Gompper on the Occasion of his 70th Birthday

Abstract. By nitrosation of the mineralic acid salts of *N*-monosubstituted 1-naphthylamines (**7**) *N*-monosubstituted *N'*-hydroxy-naphthoquinone diiminium salts (**9**) are formed. These compounds can condense with their naphthylamine educts **7** to deeply colored *N*-(4-amino-naphthyl)-substituted naphthoquinone diiminium salts **11** which are available by the reaction of the mineralic acid salts of *N*-monosubstituted 1-naphthylamines **7** with one half equivalent of nitrous acid in acetic acid solution also. The new indaminium salts **11** absorb, in contrast to their deprotonated species **12** which exhibit intense absorption bands at about 550 nm, in the near infrared region very intensively at about 820 nm.

The nitrosation of aromatic amines **1** is a well-known and intensively studied reaction which is most important for preparing organic dyes and their intermediates [1]. Depending on the conditions applied and the educts used different types of products are formed. Thus, by the reaction of *N*-unsubstituted aromatic amines **1a** ($R^1 = R^2 = H$) with nitrous acid in acidic solution aromatic diazonium salts **2** are obtained [2]. From *N*-mono-substituted aromatic amines **1b** ($R^1 \neq H$, $R^2 = H$) or *N*-disubstituted aromatic amines **1c** ($R^1 = R^2 \neq H$) *N*-nitroso or 4-nitroso anilines **3** or **4**, resp., are obtained by using the same reagent [3].

Generally, in order to obtain good yields of products, special conditions are necessary. Thus, high yields of aryl diazonium salts **2** can be obtained only at low temperatures and if a strong mineralic acid in high concentration depending on the basicity of the appropriate aniline educt **1a** is applied . To obtain high yields of 4-nitroso-anilines **4** special types of mineralic acids, like hydrochloric acid, in a definite concentration, stoiochiometric amounts of nitrous acid, and low reaction temperature have to be applied. On the contrary, to get satisfactory yields of *N*-nitroso-anilines **3** high concentrations of mineralic acid have to be avoided.



[1]) Presented at the 2nd Iminiumsalz-Tagung, Stimpfach-Rechenberg, Germany, September 20–22, 1995

In many cases, despite of these conditions several by- and consecutive products are obtained. Such products are, e.g. phenols [4], quinone imines [5] and quinone monoximes [6], 4-nitro-anilines [7], 4-nitro-*N*-nitroso-anilines [8], benzidines [9], or diphenoquinone bis-iminium salts [10] as well as diaryl triazenes [11], aminoazo and hydroxyazo benzenes [12]. In case of *N*-nitroso-anilines **3** isomeric NH-substituted 4-nitroso-anilines **4** (R^2 = H) can be formed also [3]. Whereas the last-mentioned type of compounds is formed as the result of a Fischer-Hepp rearrangement [13] the other ones can be formed, in a more or less extent, as result of hydrolytic or oxidative splitting reactions of the corresponding educts, intermediates or products.

Remarkably, a special consecutive product which should be expected in the course of the formation of 4-nitroso-anilines **4**, namely the *N*-(4-aminophenyl)-quinone diiminium salts **6**, has not been isolated as yet in a noticeable extent [14]. Such *N*-(4-aminophenyl)-quinone diiminium salts **6** can be prepared, however, in a preparative scale by oxidative coupling reaction [15] of a *N*-disubstituted aromatic amine **1c** with a *para*-phenylene diamine derivative **5** which is available, e.g. by reduction of 4-nitroso-anilines **4**.

At first glance, the variety of the products formed by the reaction of aromatic amines with nitrous acid seems independent of the kind of substituents in the aryl moieties, provided the 4-position in the aniline educts is unsubstituted and there is no large steric hindrance at this position e.g., by bulky substituents in 3-position.

However, in the course of the nitrosation of 1-naphthylamines **7** some remarkable differences with respect to the the nitrosation of anilines **1** are observed. Thus, both the unsubstituted and the *N*-monoethyl-substituted naphthylamines **7a** and **7b** are *directly* transformed by nitrous acid/concentrated sulphuric acid into the corresponding 4-nitroso derivatives **10a** and **10b**, respectively [16]. A detailed study of this reaction ruled out that it proceeds *via* the intermediate *N*-nitroso-1-naphthylamines **8**.

Because there are as yet only few 4-nitroso-derivatives **10** of *N*-mono-substituted 1-naphthylamines described in the literature we tried to prepare some further compounds of this type including the bridged 1-naphthylamine derivatives **7f** and **7g** by starting from some *N*-mono-substituted 1-naphthylamines **7** (R^1 = H) by using the nitrosation method as well in concentrated sulphuric acid (method A) as in acetic acidsolution (method B). The results obtained are summarised in table 1.

As to see, only in case of the non-bridged *N*-mono-substituted 1-naphthylamines **7a–7d** the method A gives satisfactory yields of the corresponding 4-nitroso-1-naphthylamine derivatives **10** which were advantageously isolated in the form of their mineralic acid salts. According to the analytical and spectroscopic data these salts possess a *N*-hydroxy-quinone diiminium structure **9**.

With the *N*-phenyl *N*-cyanoethyl substituted 1-naphthylamines **7c** and **7d** both the methods A and B give the 4-nitroso derivatives **9c** and **9d**, respectively,.With the bridged *N*-monosubstitued 1-naphthylamines **7f** and **7g**, however, neither the methods A nor the method B give the expected 4-nitroso compounds **10f** and **10g** or their corresponding *N*-hydroxy-naphthoquinone diiminium salts **9f** and **9g**, in satisfactory yield: Whereas the method A yields untractable tears only, the method B gives, especially if the nitrosation has been performed by using a non-sufficient amount of nitrous acid, deeply colored compounds which are, according to their analytical and spectroscopic data, *N*-(4-amino-naphthyl)-naphthoquinone diiminium salts **11**.

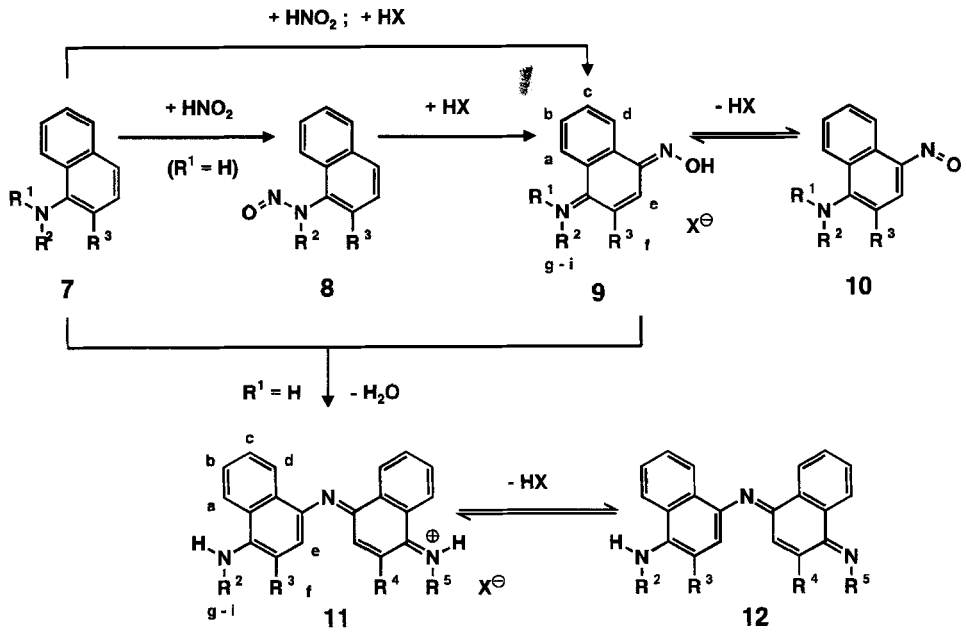
These bis-benzocondensed indaminium salts **11** were obtained in satisfactory yields if perchloric acid is added to the reaction solution or if the 1-naphthylamine educts **7** applied are used in the form of their hydroperchlorates, and the reaction mixture is heated after the addition of sodium nitrite as nitrosation reagent for few minutes. In some cases, the new *N*-(4-amino-naphthyl)-naphthoquinone diiminium salts **11** so obtained were isolated, after their recrystallization from nitromethane, as nitromethane adducts.

Table 1 Results of the nitrosation of several 1-naphthylamine derivatives **7**

				Method A		Method B		
R^1	R^2	R^3	Educt	Product	Yield	Product	Yield	m.p. [°C]
H	H	H	**7a**	**10a**	84 %[a]	[b]	–	
H	C_2H_5	H	**7b**	**10b**	73 %[a]			
				9b (X = ClO_4)	80 %	**9b** (X = ClO_4)	80 %	163–165 (X = ClO_4)
H	$(CH_2)_5COOH$	H	**7c**	**9c** (X = Cl)	75 %	**9c** (X = ClO_4)	45 %	158–159 (X = Cl)
H	C_2H_4CN	H	**7d**	**9d** (X = ClO_4)	75 %	**9d** (X = ClO_4)	70 %	160–162 (X = ClO_4)
H	C_6H_5	H	**7e**	–	–	–	–	–
H	$-(CH_2)_3-$		**7f**	–	–	–	–	–
H	$-C(CH_3)_2-CH=C(CH_3)-$		**7g**	–	–	–	–	–
CH_3	CH_3	H	**7h**	**9h** (X = ClO_4)	95 %	**9h** (X = ClO_4)	92 %	169–170 (X = ClO_4)

[a]) Lit. [16]

[b]) 1-naphthalene diazonium hydrosulfate [17]



Obviously, under the conditions applied the primary formation of 4-nitroso-1-naphthylamines **10** or their salts **9** is accompanied by the condensation of their unreacted *N*-substituted 1-naphthylamine educts **7** giving rise to the corresponding indaminium salts **11**. This hypothesis has been confirmed by the synthesis of some of the indaminium salts **11** by treatment of equimolar amounts of a *N*-substituted 1-naphthylamine derivative **7** with the analog *N*-substituted *N'*-hydroxy naphthoquinone diiminium salt **9** obtained by the nitrosation procedure A or B as described previously.

Analogously, unsymmetrical *N*-(4-amino-naphthyl)-naphthoquinone diiminium salts **11**, as exemplified by the compound **11bd**, could also be prepared by heating the *N*-substituted 1-naphthylamine derivative **7b** in acetic acid solution with the *N*-hydroxy-substituted naphthoquinone-diiminium salt **9d** variedly substituted at its *N*-atom. To distinguish from the method B this synthetic variant starting from the educts **7** and **9** is designed as method C.

In table 2 the symmetrically and unsymmetrically substituted *N*-(4-amino-naphthyl)-naphthoquinone diiminium salts **11** prepared by both the methods B and C are summarised.

Evidently, whereas the unsymmetrically substituted *N*-(4-amino-naphthyl)-naphthoquinone diiminium salt **11bd** can be prepared by means of method C only, the symmetrically substituted analogues, such as the compounds **11b** and **11d**, could be prepared by both the methods B and C.

It is worth mentioning that the bis-(*N*-phenyl)-substituted *N*-(4-amino-naphthyl)-naphthoquinone diiminium perchlorate **11e** as well as its bridged derivatives **11f** and **11g** (prepared from the corresponding bridged 1-naphthylamine derivatives 1,2,3,4-tetrahydro-benzo [h]quinoline **7f** and 2,2,4-trimethyl-1,2-dihydro-benzo [h]quinoline **7g**, resp.) can only be prepared by using strictly anaerobic conditions. Otherwise, neither the corresponding bridged 4-nitroso-1-naphthylamine precursors **9f** or **9g** (see table 1) nor the corresponding *N*-(4-amino-naphthyl)-naphthoquinone diiminium salts **11f** or **11g** could be isolated in noticeable yields. Instead, oxidation products of the starting 1-naphthylamine educts **7** or of the primarily formed indaminium salts

Table 2 N(4-Amino-naphthyl)-naphthoquinone diiminium perchlorates **11** (X = ClO_4)

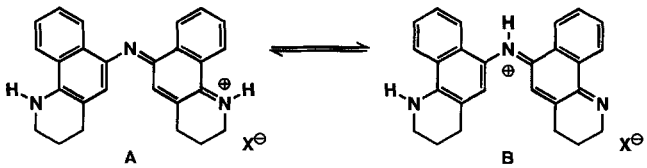
Nr.	R^2	R^3	R^4	R^5	m.p. [°C]	Yield [%] (method)
11b	C_2H_5	H	H	C_2H_5	188 – 190	77 (B); 75 (C)
11d	C_2H_4CN	H	H	C_2H_4CN	177 – 180	56 (B); 56 (C)
11e	C_6H_5	H	H	C_6H_5	188 – 190	24)B)
11f	$-(CH_2)_3-$		$-(CH_2)_3-$		178 – 180	84 (B)
11g	$-C(CH_3)_2-CH=C(CH_3)-$		$-C(CH_3)_2=CH-C(CH_3)_2-$		> 150 dec.	41 (B)
11bd	C_2H_5	H	H	C_2H_4CN	170 – 172	68 (C)

11 could be obtained. The preparation and structural characterization of the new compounds will be described in a forthcoming paper.

Difficulties arise also if the new synthesis of indaminium salts is attempted with *N,N*-disubstituted 1-naphthylamine derivatives, e.g. with *N,N*-dimethyl-1-naphthylamine **7h** or with its 4-nitroso derivative **10h**. Neither by method B nor method C the corresponding *N*-(4-amino-naphthyl)-naphthoquinone diiminium salt **11h** were obtained in crystalline form. Only deeply colored solutions could be obtained in which the expected *N*-(4-amino-naphthyl)-naphthoquinone diiminium salts **11h** formed were detected by their long-wavelength absorption maximums at about 800 nm (see table 4).

All *N*-hydroxy-quinone diiminium salts **9** and *N*-(4-amino-naphthyl)-naphthoquinone diiminium salts **11** compiled in the tables 1 and 2 are new compounds; their structures have been confirmed by means of their analytical and spectral data. Some of these data are summarised in table 3 and 4.

The ^{1}H NMR spectra of the naphthoquinone diiminium salts **9** and **11** exhibit signals at about 7.00–9.00 ppm and 1.00–4.00 ppm. Whereas the first set of signals can be attributed to the aromatic protons the second one can be attributed to the protons bound to the *N*-alkyl groups. Because in the *N*-(4-amino-naphthyl)-naphthoquinone diiminium salts **11** the same numbers of signals are found as in their nitroso educts **9** with identical *N*-substituents, it follows that these salts **11**, as exemplified for the compond **11f**, exist only in their symmetric form A and not in their unsymmetric form



11 f

B. Remarkably, neither in the salts **9** nor in the indaminium salts **11** any signals attributed to *N*-bounded protons could be detected. This fact suggests a high acidity of both the naphthoquinone diiminium salts **9** and **11** which are easily transformed, in a suitable solvent or by means of a base, into their deprotonated species **10** and **12**.

Both the naphthoquinone diiminium salts **9** and **11** exhibit characteristic UV/VIS absorption spectra. Whereas the yellow or orange-coloured *N*-hydroxy-substituted naphthoquinone diiminium salts **9** exhibit intense absorption maxima near to the blue edge of the visible region at about 400 nm the *N*-(4-amino-naphthyl)-naphthoquinone diiminium salts **11** show intense absorption maxima in the near IR region at about 810 to 880 nm.

Due to the high acidity of the NH-bounded protons in the *N*-hydroxy-substituted naphthoquinone diiminium salts **9** and *N*-(4-amino-naphthyl)-naphthoquinone diiminium salts **11** both these salts can be transferred

Table 3 Characteristic ^{1}H NMR and IR data of the N-hydroxy-naphthoquinone diiminium salts (**9**) and N-(4-amino-naphthyl)-naphthoquinone diiminium perchlorates (**11**); chemical shift in ppm (assignment); IR absorption, in cm^{-1} (assignment)

Pos.	**9b**	**9c**	**9d**	**11b**	**11d**	**11e**	**11f**	**11bd**	
a	8.45 (d)	8.78 (dd)	8.42 (d)	8.63 (d)	8.64 (d)	8.86 (d)	8.63 (d)	8.74 (d)	8.84 (d)
b	7.82 (t)	7.86 (t)	7.82 (t)	7.72 (t)	7.82 (t)	7.92 (t)	7.69 (t)	7.80 (t)	8.14 (t)
c	7.91 (t)	7.92 (t)	7.89 t)	7.76 (t)	7.78 (t)	7.84 (t)	7.77 (t)	7.71 (t)	8.05 (t)
d	8.39 (d)	8.38 (dd)	8.37 (d)	8.37 (d)	8.41 (d)	8.33 (d)	8.28 (d)	8.41(d)	8.60 (d)
e	8.16 (d)	8.14 (d)	8.11 (d)	7.37 (d)	7.33 (d)	7.48 (d)	7.23 (s)	7.16d)	7.42d)
f	7.63 (d)	7.64 (d)	7.65 (d)	7.18 (d)	7.21 (d)	7.39 (d)	–	7.13 (d)	7.39d)
g	3.99 (q)	3.97 (t)	4.24 (t)	3.69 (q)	3.94 (t)	7.55 (m)	3.69 (t)	3.78 (q)	3.96 (t)
h	1.36 (t)	1.50 (m)	3.07 (t)	1.36 (t)	3.02 (t)		1.98 (m)	1.49 (t)	3.01 (t)
i		2.23 (t)					2.93 (t)		
IR		1725 (CO)	2250 (CN)	3250 (NH)	3300 (NH) 2250 (CN)	3250 (NH)	3250 (NH)	3300 (NH) 2250 (CN)	

Table 4 Longest-wavelength absorption maxima of the *N*-(4-amino-naphthyl)-naphthoquinone diiminium perchlorates (**11**) and their corresponding deprotonated species **12**

	11b	**11d**	**11e**	**11f**	**11g**	**11bd**	**11h**
λ_{max} [nm][a]	814	812	845	830	880	810	800
log ε	4.93	4.29	4.85	4.98		4.62	
	12b	**12d**	**12e**	**12f**	**12g**	**12bd**	**12h**
λ_{max}[nm][b]	555	550	540	585	600	558	–

[a]) in methylene chloride
[b]) in acetonitrile

into their corresponding non-protonated species relatively easily, e.g. by means of weak bases. This transformation can be unambiguously spectroscopically detected. Whereas in the 4-nitroso-1-naphthylamine series **9** or **10** the absorption maxima are not strongly shifted to shorter wavelength on going from the protonated to deprotonated species the maxima of the *N*-(4-amino-naphthyl)-naphthoquinone diiminium salts **11** are extremely shifted to shorter wavelengths by deprotonation to give the species **12**. In accordance with table 4 and fig. 1, in which the absorption spectra of the cationic and neutral form of the bridged *N*-(4-amino-naphthyl)-naphthoquinone diiminium salts **11f** are shown, the colour of this compound changes from pale green to intensive purple. The bright green colour of the *N*-(4-amino-naphthyl)-naphthoquinone diiminium salts **11f** originates from the absence of any absorption band with significant intensity in the visible spectral range. Therefore, solutions of the *N*-(4-amino-naphthyl)-naphthoquinone diiminium salt **11f** appear, in contrast to those of

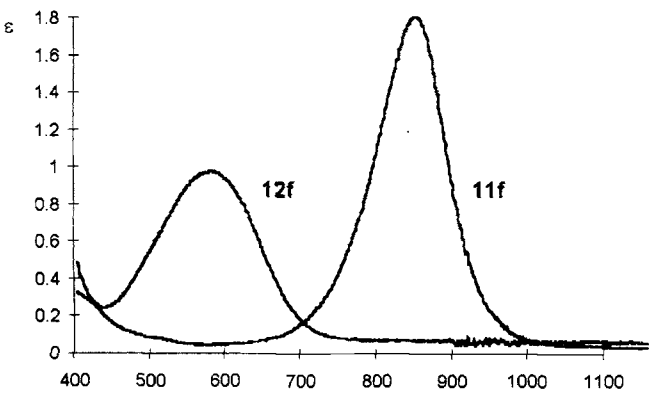


Fig. 1 Absorption spectra of *N*-(4-amino-naphthyl)-naphthoquinone diiminium perchlorate **11f** and its deprotonated form **12f**

the neutral compound **12f**, visually nearly colourless. Due to these properties the *N*-(4-amino-naphthyl)-naphthoquinone diiminium salts **11** can be used in several different fields of application, e.g., in energy transfer and storage systems, in information recording and display systems, or in medical and biological fields [18, 19]. Furthermore, they can be used as IR absorber for automatic identifications or heat-ray blocking [20] or as IR active pH-indicators [21]. Such indicators receive, at present, a lot of interest because they can be advantageously used to indicate proton concentrations in biological materials which are usually highly transparent in the near IR region [22].

The authors thank the BAYER AG for financial support of this work.

Experimental

Melting points were determined by using a Boëtius heating-block microscope and are corrected. The IR spectra were recorded in potassium bromide pellets with a Philips FTIR spectrometer PU 9624, the visible and near infrared spectra with a Shimadzu spectrometer UV 3101, and the NMR spectra with a Varian 300 MHz spectrometer Gemini 300 or with a JEOL 200 MHz spectrometer JNM FX 200. The elemental analytical data were obtained by using a LECO analyser CHNS 932. All dye-forming reactions were monitored by means of thin-layer chromatography using 0.2 mm silica plates (Merck). The naphthylamine educts **7a, 7b,** and **7e** used are commercially available. The bridged 1-naphthylamine derivative **7g** and the cyanoethyl-substituted 1-naphthylamine derivative **7d** were prepared according to the literature [23, 24]. The bridged 1-naphthylamine derivative 1,2,3,4-tetrahydro-benzo[h] quinoline **7f** was prepared in form of its hydroperchlorate **7d**·$HClO_4$ as follows.

1,2,3,4-Tetrahydro-benzo[h]quinoline hydroperchlorate **7f**·$HClO_4$

A mixture of 0.2 mol (28,6 g) 1-naphthylamine, 0.6 mol (94,5 g) 1-bromo-3-chloro-propane, and 0.1 mol (10.6 g) sodium carbonate was heated with stirring for 2 h at 60 °C, than at 120 °C until no starting 1-naphthylamine could be detected by thin-layer chromatography after coupling with 4-nitrobenzene diazonium salt solution. Then the unreacted 1-bromo-3-chloro-propane was separated from the reaction mixture by destillation at 190 °C. After cooling the resulting mixture was neutralised with ammonia and extracted with ether. After addition of aqueous perchloric acid (70%) to the ether extract the title compound precipitates and can be isolated by suction in a yield of 80%.White crystals; m.p. 188–190 °C; ^1H NMR (DMSO-D_6): δ = 2.04 (q, 2H, CH_2), 2.97 (t, 2H, CH_2), 3.54 (t, 2H, CH_2), 4.80 (s, 2H, NH_2), 7.35 (d, 1H, CH-6), 7.58 (t, 1H, CH-9), 7.67 (t, 1H, CH-8), 7.78 (d, 1H, CH-5), 7.94 (d, 1H, CH-7), 7.96 (d, 1H, CH-10).
$C_{13}H_{14}ClNO_4$ (283.7): calcd.: C 55.04, H 4.97, N 4.94; found C 55.17, H 4.74 N 5.12.

Nitrosation of *N*-monosubstituted 1-naphthylamines 7 (general procedure)

Method A:
To 150 g concentrated sulphuric acid 0.1 mol (7.0 g) sodium nitrite and, after 1 h, 0.1 mol of a *N*-monosubstituted 1-naphthylamine **7** (or its mineralic acid salt) is added at 0 °C. After stirring for 10 h at this temperature the reaction mixture is poured on ice mixed with 200 ml of hydrochloric or perchloric acid in order to precipitate the N-hydroxy-naphthoquinone diiminium salt **9** formed. It can be isolated by suction and purified by recrystallization from ethanol.

Method B:
To 0.1 mol of the corresponding 1-naphthylamine **7** (or its hydroperchlorate), solved in 50 ml acetic acid, 0.1 mol (7.0 g) sodium nitrite was added in small portions. After stirring the reaction mixture for 1 h the mineralic acid salts **9** of the nitroso compound **10** precipitate after addition of perchloric acid and water, and are isolated by suction.

N-(4-amino-naphthyl)-naphthoquinone diiminium salts (11) (general procedure)

Method B:
To a mixture of 0.02 mol of a *N*-monosubstituted 1-naphthylamine **7** (or its hydroperchlorate **7**·$HClO_4$) in 50 ml acetic acid 0.01 mol (0.7 g) sodium nitrite is added with stirring. Then, so far as no 1-naphthylamine hydroperchlorate is used, 1.5 ml perchloric acid (70%) is added to the reaction mixture which is refluxed for 5 min. After cooling the *N*-(4-amino-naphthyl)-naphthoquinone diiminium salts **11** formed crystallize and are isolated by suction. They are pruified by recrystallisation from nitromethane which gives a 1:1 adduct.

Method C:
0.01 mol of a *N*-mono-substituted 1-naphthylamine **7** and 0.01 mol of its corresponding *N*-hydroxy-naphthoquinone diiminium perchlorate **9** are solved in 50 ml ethanol or acetic acid. The resulting mixture is refluxed for 5 min and then cooled. The products crystallize, and are isolated and purified as described before.

The elemental analytical data of all compounds prepared are in satisfactory agreement with the calculated ones.

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