



Nucleophilic Substitution on Arylazo Compounds: Part IV. Reactions of Chloro-Substituted Arylazonaphthalenes with Primary and Secondary Amines*

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ABSTRACT

In 2- and 4-chloro-substituted arylazonaphthalenes the naphthalene-linked halogen can be substituted by different primary and secondary amines giving rise to the formation of a wide variety of N-mono- and N-disubstituted 1-arylazo-2- or 4-naphthylamines, 1-arylamino-1H-naphth(1,2-d)imidazoles, and N,N-disubstituted 5-amino-3H-naphth(1,2-d)imidazoles. Whereas for the formation of the arylazo naphthylamines a common nucleophilic substitution path is assumed, a redox mechanism seems to be operative for the formation of the azo-group-free naphth(1,2-d)imidazoles.

1 INTRODUCTION

Arylazo-substituted naphthylamines are useful as dyes for different materials, especially for textile fibres such as cotton and silk. For these purposes the dyes used must be water-soluble to some extent and, therefore, they must be functionalized by hydrophilic groups, such as SO_3^- .

A common method of preparing such water-soluble arylazo-substituted naphthylamines is the coupling of an aryldiazonium salt with 1- or 2-naphthylamines containing hydrophilic groups.⁴

* Parts I, II, and III: see Refs 1, 2 and 3, respectively.

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In recent years arylazo-substituted naphthylamines having good solubility in non-polar media have also become of interest, such dyes being useful, e.g. for dyeing polyester fibres^{5,6} or for enhancing the contrast of nematic materials in liquid crystal displays.⁷

The preparation of hydrophobic arylazonaphthylamines follows the general route for preparing the water-soluble analogues and thus requires the use of naphthylamines free of hydrophilic groups. Many such compounds are, however, suspect for ecological reasons or because of potential carcinogenic activity.⁸

An alternative way of preparing arylazo-substituted naphthylamines with good solubility in non-polar media is the nucleophilic substitution of halogen in chloro-substituted arylazonaphthalenes by amines. The nucleophilic substitution of halogen in arylazo compounds is a relatively undeveloped method for preparing amino-substituted arylazo compounds⁹ and the halogen-substituted arylazonaphthalenes required for this reaction are almost unknown.

In 1987 we published, however, a simple and general method for preparing chloro-substituted arylazonaphthalenes **3** and **4**. It consists in the reaction of arylazo naphthols **1** and **2**, with POCl₃ in the presence of dimethylformamide.¹ The educts required for this transformation are readily available by coupling an appropriate aryl diazonium salt with 1- or 2-naphthol.⁴

In this publication we summarize results concerning the nucleophilic substitution of halogen in the chloro-substituted arylazonaphthalenes **3** and **4** by amines.

2 RESULTS AND DISCUSSION

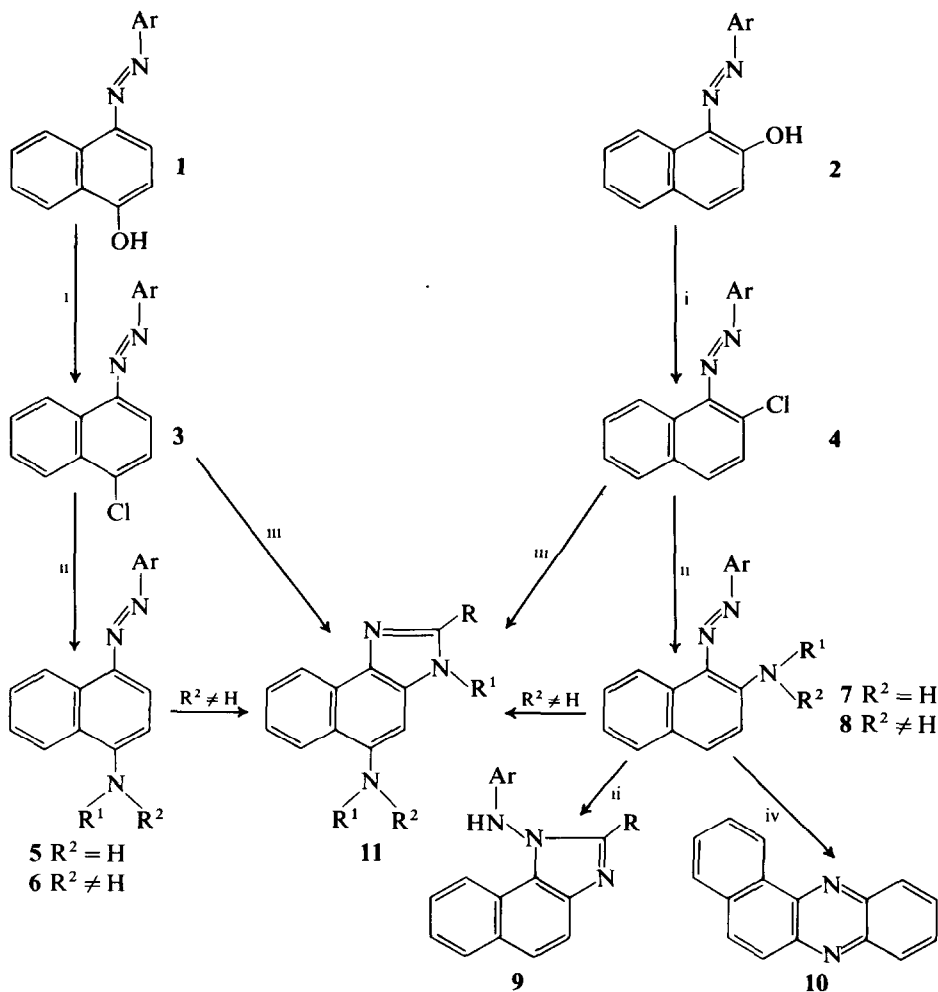
2.1 Reaction of chloro-substituted arylazonaphthalenes with primary amines

The most positive results for nucleophilic substitution of halogen in the chloro-substituted arylazonaphthalenes **3** and **4** were obtained with primary amines, using the 1-arylazo-4-chloronaphthalenes **3**.

If both the educts are mixed and heated together at about 100°C in an aprotic dipolar solvent such as acetonitrile or dimethylformamide (method A), or with an excess of the appropriate amine without any further solvent at the reflux temperature of the amine (method B), nucleophilic substitution of the chlorine takes place giving rise to the formation of 1-arylazo-4-naphthylamines **5**.

Table 1 shows the examples studied and the results obtained.

The substitution of halogen occurs relatively quickly and without com-



(i) POCl_3/DMF ; (ii) H_2NR_1 ; HNR_1R_2 (method A, in DMF; method B, without any solvent); (iii) $\text{HNR}_1\text{R}_2/\text{DMF}$; (iv) mineral acid.

Scheme 1

plication if the arylazo educts **3** (Scheme 1) are substituted by electron-acceptor groups in the aryl moiety, whereas a slower substitution takes place with donor-substituted analogues. The reaction products can, in general, be isolated by filtering after cooling and addition of methanol to the reaction mixture. There are no significant differences between the results obtained with aliphatic or aromatic primary amines as reagents, except when acceptor-substituted anilines are used.

Similar results were also obtained by the reaction of the isomeric 1-aryldiazo-2-chloronaphthalenes (**4**) with primary amines. The expected substitution products of the general formula **7** occur only, however, if

TABLE 1
Results of the Conversion of 1-Arylozo-4-chloronaphthalenes **3** into 1-Arylozo-4-naphthylamines **5** and Melting points and UV/Vis Absorption Spectral Data (Measured in Dimethylformamide) of these 1-Arylozo-4-naphthylamines **5**

Compound	Ar	R	Method	Reaction time (h)	Yield (%)	M.p. (°C)	λ_{\max} (nm) (log ϵ) ^a
5.1	4-NO ₂ -C ₆ H ₄	C ₆ H ₅	B	5	53.0	188	516 (4.23)
5.2	4-NO ₂ -C ₆ H ₄	4-CH ₃ -C ₆ H ₄	A	6	55.0	141-142	517 (4.22)
5.3	4-NO ₂ -C ₆ H ₄	4-CH ₃ O-C ₆ H ₄	A	6	55.5	167	518 (4.24)
5.4	2,4-(NO ₂) ₂ -C ₆ H ₃	C ₆ H ₅	B	6	58.5	179	546 (4.29)
5.5	2,4-(NO ₂) ₂ -C ₆ H ₃	4-CH ₃ -C ₆ H ₄	A	7	57.0	181	548 (4.27)
5.6	2,4-(NO ₂) ₂ -C ₆ H ₃	4-CH ₃ O-C ₆ H ₄	A	7	57.0	162-163	549 (4.28)
5.7	2-CN-4-NO ₂ -C ₆ H ₃	C ₆ H ₅	B	6	54.0	163-164	559 (4.29)
5.8	2-CN-4-NO ₂ -C ₆ H ₃	4-CH ₃ -C ₆ H ₄	A	7	59.0	172-173	561 (4.28)
5.9	2-CN-4-NO ₂ -C ₆ H ₃	4-CH ₃ O-C ₆ H ₄	A	7	61.0	151	563 (4.30)
5.10	4-NO ₂ -C ₆ H ₄	<i>n</i> -C ₄ H ₉	A	1	59.5	155	529 (4.27)
5.11	4-NO ₂ -C ₆ H ₄	<i>n</i> -C ₆ H ₁₃	A	1	58.5	213-214	531 (4.28)
5.12	4-NO ₂ -C ₆ H ₄	<i>n</i> -C ₈ H ₁₇	A	1	57.0	196	531 (4.28)
5.13	4-NO ₂ -C ₆ H ₄	<i>c</i> -C ₆ H ₁₁	A	2.5	58.5	281-283	528 (4.29)
5.14	4-NO ₂ -C ₆ H ₄	C ₆ H ₅ -CH ₂	B	3	57.0	183-185	518 (4.26)
5.15	2,4-(NO ₂) ₂ -C ₆ H ₃	<i>n</i> -C ₄ H ₉	A	1	60.5	210	558 (4.31)
5.16	2,4-(NO ₂) ₂ -C ₆ H ₃	<i>n</i> -C ₆ H ₁₃	A	1	58.0	243-245	560 (4.30)
5.17	2,4-(NO ₂) ₂ -C ₆ H ₃	<i>n</i> -C ₈ H ₁₇	A	1	57.0	215	563 (4.31)
5.18	2,4-(NO ₂) ₂ -C ₆ H ₃	<i>c</i> -C ₆ H ₁₁	A	3	52.0	240-242	555 (4.30)

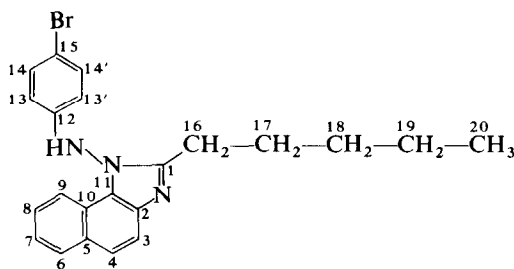
5.19	2,4-(NO ₂) ₂ -C ₆ H ₃	C ₆ H ₅ -CH ₂	B	3.5	56.5	253-255	547 (4.30)
5.20	2-CN-4-NO ₂ -C ₆ H ₃	n-C ₄ H ₉	A	1	60.0	213	569 (4.31)
5.21	2-CN-4-NO ₂ -C ₆ H ₃	n-C ₆ H ₁₃	A	1	59.0	201-203	571 (4.31)
5.22	2-CN-4-NO ₂ -C ₆ H ₃	n-C ₈ H ₁₇	A	1	57.5	209	573 (4.32)
5.23	2-CN-4-NO ₂ -C ₆ H ₃	n-C ₆ H ₁₁	A	3.5	55.0	263-265	570 (4.30)
5.24	2-CN-4-NO ₂ -C ₆ H ₃	C ₆ H ₅ -CH ₂	B	3.5	57.0	261-264	559 (4.29)
5.25	2-Benzothiazolyl	n-C ₄ H ₉	A	1	51.0	230	469 (4.25)
5.26	2-Benzothiazolyl	n-C ₆ H ₁₃	A	1	50.0	214	471 (4.23)
5.27	2-Benzothiazolyl	n-C ₈ H ₁₇	A	1	51.5	234-236	475 (4.24)
5.28	2-Benzothiazolyl	n-C ₆ H ₁₁	A	3	53.5	217-221	471 (4.24)
5.29	2-Benzothiazolyl	C ₆ H ₅ -CH ₂	B	3	51.0	216	457 (4.26)
5.30	2-Benzothiazolyl	C ₆ H ₅	B	6	49.5	149-151	455 (4.24)
5.31	2-Benzothiazolyl	CH ₃ -C ₆ H ₄	A	5	50.5	167	458 (4.22)
5.32	2-Benzothiazolyl	CH ₃ O-C ₆ H ₄	A	6	50.5	174	461 (4.22)
5.33	4-Cl-C ₆ H ₄	C ₆ H ₅	B	6	49.5	151-153	456 (4.22)
5.34	4-Cl-C ₆ H ₄	CH ₃ -C ₆ H ₄	A	6	50.0	142	458 (4.21)
5.35	4-Cl-C ₆ H ₄	CH ₃ O-C ₆ H ₄	A	7	51.0	152	459 (4.21)
5.36	4-Cl-C ₆ H ₄	n-C ₁₂ H ₂₅	A	2	59.5	198	467 (4.23)
5.37	4-NO ₂ -C ₆ H ₄	n-C ₁₂ H ₂₅	A	2	62.5	219	529 (4.26)
5.38	2,4-(NO ₂) ₂ -C ₆ H ₃	n-C ₁₂ H ₂₅	A	2	63.0	205-207	560 (4.30)
5.39	2-CN-4-NO ₂ -C ₆ H ₃	n-C ₁₂ H ₂₅	A	2	63.5	198-199	571 (4.31)

^a UV/Vis absorption spectra were measured in DMF.

TABLE 2

¹H- and ¹³C-NMR Data of 2-Pentyl-1-(4-bromophenyl)-amino-1*H*-naphth(1,2-*d*)imidazole **9.3**^a

¹³ C-δ (ppm) (Multiplicity)	¹ H-δ (ppm) (Assignment)
C-1 155.0 (m)	0.80 (—CH ₃ at C-20)
C-2 138.2 (d)	1.30 (—CH ₂ — at C-19)
C-3 119.9 (s)	1.80 (—CH ₂ — at C-18)
C-4 120.3 (d)	2.03 (—CH ₂ — at C-17)
C-5 125.2 (t)	2.93 (—CH ₂ — at C-16)
C-6 128.9 (t)	6.61 (benzo- <i>H</i> ,2 <i>H</i> at C-13, C-13')
C-7 125.8 (d)	7.22 (benzo- <i>H</i> ,2 <i>H</i> at C-14, C-14')
C-8 124.3 (d)	7.40–8.47 (naphtho- <i>H</i> ,6 <i>H</i> at C-3, C-4, C-6–C-9)
C-9 123.4 (d)	9.36 (—NH—)
C-10 121.6 (t)	
C-11 127.6 (t)	
C-12 146.0 (t)	
C-13 113.9 (d)	
C-14 129.6 (d)	
C-15 131.3 (t)	
C-16 31.6	
C-17 27.1	
C-18 26.1	
C-19 22.3	
C-20 13.5	

^a Measured in DMSO-*d*₆.

primary aromatic amines or aliphatic amines with a lower alkyl group and no solvent are used. With long-chain aliphatic primary amines, no *N*-substituted 1-arylo-2-naphthylamines **7** could be obtained, only azo-group-free products being isolated.

For elucidation of the structure of these products ¹H- and ¹³C-NMR was used. As shown for the reaction product of the arylazo compound **4** with (for example) *n*-pentylamine (see Table 2), all signals measured could be assigned to the proton and carbon atoms for a compound which has an *N*-arylamino-naphtho(1,2-*d*)imidazole structure corresponding to formula **9**.

Table 3 shows the 1-arylo-2-naphthylamines **7** prepared, and Table 4 the naphtho(1,2-*d*)imidazoles **9** obtained by the reaction of the 1-arylo-2-chloronaphthalenes **4** with longer-chain alkylamines.

The formation of the heterocyclic compounds **9** is somewhat surprising, but it could be explained according to a similar mechanism occurring in the reaction of 1-arylo-2-naphthylamines with aromatic aldehydes¹⁰ by an intramolecular hydrogen transfer running from the α-carbon atom of the alkyl group of the amine to the azo moiety.

TABLE 3

Results of the Conversion of 1-Arylazo-2-chloronaphthalenes **4** into 1-Arylazo-2-aminonaphthalenes **7** and Melting Points and UV/Vis Absorption Spectral Data (Measured in DMF) of these 1-Arylazo-2-aminonaphthalenes **7**

Compound	Ar	R	Method	Reaction time (h)	Yield (%)	M.p. (°C) (Lit.)	λ_{\max} (nm) (log ϵ) ^a
7.1	4-NO ₂ -C ₆ H ₄	<i>n</i> -C ₃ H ₇	B	12	61.0	260	538 (4.29)
7.2	4-NO ₂ -C ₆ H ₄	C ₆ H ₅	B	13	64.0	216 (217-218) ^b	526 (4.28)
7.3	4-NO ₂ -C ₆ H ₄	2,4-(NO ₂) ₂ -C ₆ H ₃	A	14	61.5	230	522 (4.29)
7.4	2,4-(NO ₂) ₂ -C ₆ H ₃	C ₆ H ₅	B	13	61.5	253-255	556 (4.31)
7.5	2-CN-4-NO ₂ -C ₆ H ₃	<i>n</i> -C ₃ H ₇	B	12	60.5	286	578 (4.34)
7.6	2-CN-4-NO ₂ -C ₆ H ₃	C ₆ H ₅	B	12	64.5	261-263	566 (4.30)
7.7	C ₆ H ₅	C ₆ H ₅	B	14	58.5	139-140 (141-142) ^c	446 (4.20)
7.8	C ₆ H ₅	4-CH ₃ -C ₆ H ₄	A	14	54.0	152 (152) ^d	447 (4.21)
7.9	C ₆ H ₅	2,4-(NO ₂) ₂ -C ₆ H ₃	A	14	53.0	281 (285) ^e	442 (4.19)
7.10	4-CH ₃ -C ₆ H ₄	C ₆ H ₅	B	13.5	50.5	118-120 (120) ^d	456 (4.21)
7.11	4-CH ₃ -C ₆ H ₄	2,4-(NO ₂) ₂ -C ₆ H ₃	A	14	51.0	279 (280) ^e	458 (4.21)
7.12	4-Br-C ₆ H ₄	2,4-(NO ₂) ₂ -C ₆ H ₃	A	11	51.5	261-262 (263) ^e	466 (4.21)
7.13	4-Cl-C ₆ H ₄	2,4-(NO ₂) ₂ -C ₆ H ₃	A	11	50.0	276 (278) ^e	467 (4.22)

^a UV/Vis absorption spectra were measured in DMF.

^b Ref. 17.

^c Ref. 18.

^d Ref. 19.

^e Ref. 20.

TABLE 4
 Results of the Conversion of 1-Arylazo-2-naphthylamines **7** into 2-Substituted 1-Arylamino-1*H*-naphth(1,2-*d*)imidazoles **9** and Melting Points and UV/Vis Absorption Spectral Data of these 2-Substituted 1-Arylamino-1*H*-naphth(1,2-*d*)imidazoles **9**

Compound	Ar	R	Reaction time (h)	Yield (%)	M.p. (°C) (Lit.)	λ_{\max} (nm) ($\log \epsilon$) ^b
9.1	C ₆ H ₅	C ₆ H ₅	9	63.0 62.0 ^a	198–199 (199) ^a	335 (3.49)
9.2	4-Cl-C ₆ H ₄	<i>n</i> -C ₅ H ₁₁	8	58.0	196	332 (3.66)
9.3	4-Br-C ₆ H ₄	<i>n</i> -C ₅ H ₁₁	7	62.0	185	332 (3.62)
9.4	4-Br-C ₆ H ₄	<i>n</i> -C ₉ H ₁₉	10	12.0	78	333 (3.50)

^a Prepared from 1-phenylazo-2-naphthylamine and benzaldehyde accordingly to Ref. 10.

^b UV/Vis absorption spectra were measured in DMF.

TABLE 5

Results of the Conversion of *N*-Aryl-substituted 1-Arylazo-2-naphthylamines **7** into Benzo(*b*)phenazines **10**

Product	Educt	Reaction time (h)	Yield (%)	M.p. (°C) (Lit.)	λ_{\max} (nm) (log ϵ)
10.1	7.2	2	79.0	142 (141) ^a	400 (4.08) (400, 4.08) ^b
	7.4	1.5	75.5		
	7.6	1.5	81.0		
	7.7	2.5	80.0		
	7.10	2.5	76.5		
10.2	7.3	2	75.5	198	408 (4.06)
	7.9	2	78.5		
	7.11	2	82.0		
	7.12	2	79.5		
	7.13	2	76.5		
10.3	7.8	2	80.5	213 (213) ^a	404 (4.03)

^a Ref. 21.

^b Ref. 22.

With respect to the structural elucidation of the substitution products obtained, it must be mentioned that *N*-aryl-substituted 1-arylazo-2-naphthylamines **7**, which are obtained from the chloro-substituted arylazonaphthalenes **4** by reaction with aromatic amines, can be transformed into benzo(*b*)phenazines **10** by refluxing with mineral acid, e.g. conc. hydrochloric acid, as shown previously by other authors.¹¹ Even in this case a redox step has to be operative for the formation of the product **10**. Table 5 shows the benzo(*b*)phenazines **10** prepared.

2.2 Reaction of chloro-substituted arylazonaphthalenes with secondary amines

Using secondary amines for the nucleophilic substitution of halogen in the 1-arylazo-4-chloronaphthalenes **3** and the 1-arylazo-2-chloronaphthalenes **4**, some further complications occur. If the components required are allowed to react similarly to the substitution procedure of primary amines with 1-arylazo-4-chloronaphthalenes **3**, only the expected 1-arylazo-4-naphthylamines **6** can be isolated without problems. The results obtained are summarized in Table 6.

The reaction of secondary amines with the isomeric 1-arylazo-2-chloronaphthalenes **4** leads generally to deeply coloured solutions which, instead of the expected *N,N*-disubstituted 1-arylazo-2-naphthylamines **8**,

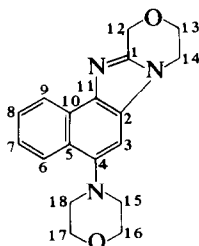
TABLE 6
 Results of the Conversion of 1-Arylazo-4-chloronaphthalenes **3** into 1-Arylazo-4-aminonaphthalenes **6** and Melting Points and UV/Vis-Absorption Spectral Data (Measured in DMF) of these 1-Arylazo-4-aminonaphthalenes **6**

Compound	Ar	NR ¹ R ²	Reaction time (h)	Yield (%)	M.p. (°C)	λ_{\max} (nm) (log ϵ) ^a
6.1	4-Cl—C ₆ H ₄	Morpholino	0.5	38.5	235	488 (4.25)
6.2	4-Cl—C ₆ H ₄	Piperidino	0.5	41.0	281	493 (4.24)
6.3	4-Br—C ₆ H ₄	Morpholino	0.5	35.5	260	486 (4.23)
6.4	4-Br—C ₆ H ₄	Piperidino	0.5	37.0	287	495 (4.24)
6.5	4-NO ₂ —C ₆ H ₄	Morpholino	0.5	48.5	213	553 (4.29)
6.6	2,4-(NO ₂) ₂ —C ₆ H ₃	Morpholino	0.5	51.5	187	587 (4.31)

^a UV/Vis absorption spectra were measured in DMF.

TABLE 7
¹H- and ¹³C-NMR Data for 5-Morpholino-3*H*-naphth(1,2-*d*)imidazole **11**.^a

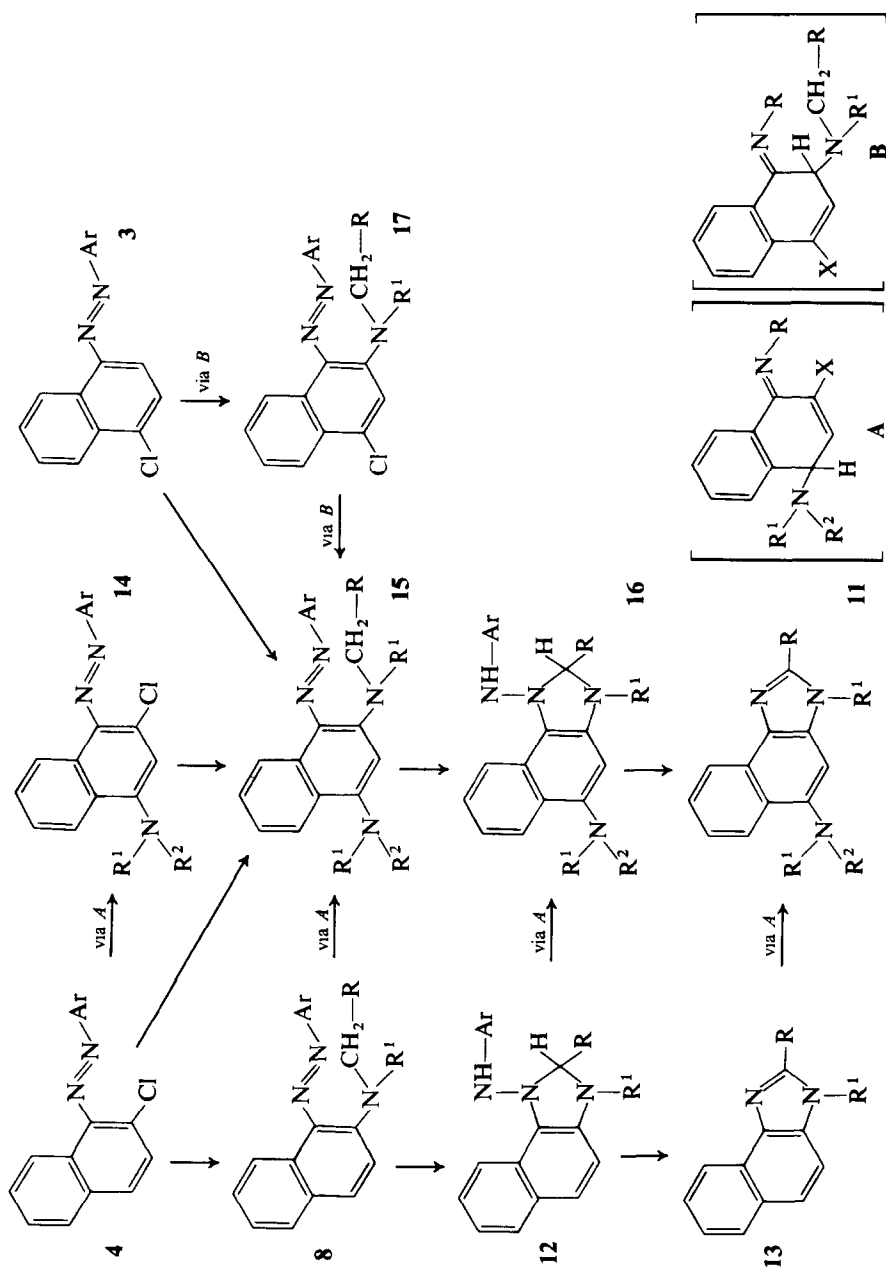
¹³ C-δ (ppm) (Multiplicity)	¹ H-δ (ppm) (Assignment)
C-1 145.1 (m)	3.09 (N—CH ₂ —, 2 × 2H at C-15, C-18)
C-2 129.8 (s)	3.94 (O—CH ₂ —, 2 × 2H at C-16, C-17)
C-3 100.4 (s)	4.28 (N—CH ₂ —CH ₂ —O, 4H at C-13, C-14)
C-4 145.1 (d)	5.00 (=C—CH ₂ —O, 2H at C-12)
C-5 128.9 (q)	7.40–7.68 (naphthalenic bonded, 3H)
C-6 123.7 (d)	8.31–8.58 (naphthalenic bonded, 2H)
C-7 126.1 (d)	
C-8 124.3 (d)	
C-9 127.1 (d)	
C-10 125.5 (t)	
C-11 134.2 (t)	
C-12 64.1	
C-13 65.4	
C-14 42.6	
C-15 54.4	
C-16 67.3	
C-17 67.3	
C-18 54.4	



^a Measured in DMSO-d₆.

contain a mixture of products, the structure of which we have not, until now, tried to elucidate. In certain cases, however, especially by using cyclic secondary amines and by refluxing the educts in dimethylformamide for a longer time, definite products could be isolated from both the chloro-substituted azo educts **3** and **4**. On the basis of their lack of colour, and on their analytical data, these products were concluded to have neither an azo nor an aryl moiety. Moreover, identically substituted products were obtained when the isomeric arylazo-substituted 2-chloro- or 4-chloronaphthalenes **3** or **4** were used for the reaction with the same secondary amine. Structural elucidation of the products by means of ¹H- and ¹³C-NMR also shows, as depicted for one example in Table 7, a naphtho-1,2-*d*)imidazole structure. The characteristic feature of this heterocyclic structure, which can be represented by the general formula **11**, is the presence of an *N,N*-disubstituted amino group linked at the 5-position of the condensed heterocyclic system. This amino group derives, obviously, from the amine reagent used for the nucleophilic substitution of halogen in the azo educts **3** or **4**.

In Table 8 the *N,N*-disubstituted 5-aminonaphtho(1,2-*d*)imidazoles **11** obtained from the 1-arylazo-2-chloro- or 4-chloronaphthalenes **3** or **4** are listed. The formation of these heterocyclic compounds **11** could be explained



Scheme 2

TABLE 8

Results of the Conversion of 1-Arylazo-4-chloronaphthalenes **3** and 1-Arylazo-2-chloronaphthalenes **4** into 5-Amino-3*H*-naphth(1,2-*d*)-imidazoles **11** and Melting Points and UV/Vis Absorption Spectral Data of these 5-Amino-3*H*-naphth(1,2-*d*)-imidazoles **11**

<i>Educt</i>	<i>Amine</i>	<i>Reaction time (h)</i>	<i>Yield (%)</i>	<i>Product</i>	<i>M.p. (°C)</i>	<i>λ_{max} (nm) (log ε)^a</i>
3.1	Morpholino	12	50.0	11.1	134	338 (3.85)
4.1	Morpholino	12	52.0			
3.2	Piperidino	14	52.0	11.2	141	341 (3.81)
4.2	Piperidino	11	52.5			
3.3	Pyrrolidino	14	48.0	11.3	187	344 (3.85)
4.3	Pyrrolidino	12	53.0			
3.4	sec.-Butyl	20	20.0	11.4	69	335 (3.80)
4.4	sec.-Butyl	15	22.5			

^a UV/Vis absorption spectra were measured in DMF.

similarly to the mechanism discussed previously with respect to the formation of the *N*-arylamino-substituted naphtho(1,2-*d*)imidazones **9**, assuming that intermediates of the structure **12–17** (Scheme 2) are possible precursors for a reaction path which includes an essential hydrogen transfer step for **8** to **12** or from **15** to **16**.

However, no information could be derived as to whether the compounds **12–17** are really precursors and what kind of detailed reaction mechanism is pertinent to their formation. Surely, a redox mechanism must be operative even for the generation of the products described. It is probably initiated by an electron transfer step incorporating the electron-rich amine on the one hand and the electron-accepting arylazonaphthalene on the other. The mechanism could, therefore, incorporate adducts of the general structure **A** or **B**, which could result from a recombination step of the radical ion precursor. The electron transfer is favoured by the low ionization potential of the amine and a high electron affinity of the arylazo compound.¹² In accord with this hypothesis, the highest yield of the amino-substituted naphtho(1,2-*d*)imidazoles **11** is obtained starting with arylazo educts substituted in their aryl moiety by electron-acceptor groups.

2.3 Spectroscopic properties of the arylazonaphthylamines

In accordance with data reported in the literature^{13,14} on similarly substituted arylazonaphthylamines, the 1-arylazo-4-naphthylamines **5** and **6** and the 1-arylazo-2-naphthylamines **7** are, in general, deeply coloured compounds which exhibit, as shown in Tables 1 and 6, and in Fig. 1, longest-wavelength absorption maxima between 455 and 578 nm with molar extinction coefficients larger than $10^4 \text{ mol litre}^{-1} \text{ cm}^{-2}$. Whereas there are no significant differences between the position of the long-wavelength absorption maxima of analogously substituted 1-arylazo-4-naphthylamines **5** and 1-arylazo-2-naphthylamines **7** (compare the spectral data for compounds **5.1**, **5.4** and **5.7** with the data for compounds **7.2**, **7.4** and **7.6**), there are significant differences between the variously phenyl-substituted derivatives of the same series **5** and **7**. Both donor and acceptor substituents produce a red shift of the long-wavelength absorption maxima, but acceptor substituents give rise to a larger bathochromic shift of up to 120 nm.

PPP calculations provide a satisfactory description of the absorption properties of differently substituted representatives of the 1-arylazo-2- and -4-naphthylamines **5**, **6** and **7**. In Fig. 1 the observed and calculated UV/Vis absorption spectral data for compounds **5.36**, **5.37** and **5.38** are depicted as examples.

Furthermore, the amino-substituted arylazonaphthalenes **5**, **6** and **7** have, as expected, fairly good solubility in non-polar solvents, such as liquid

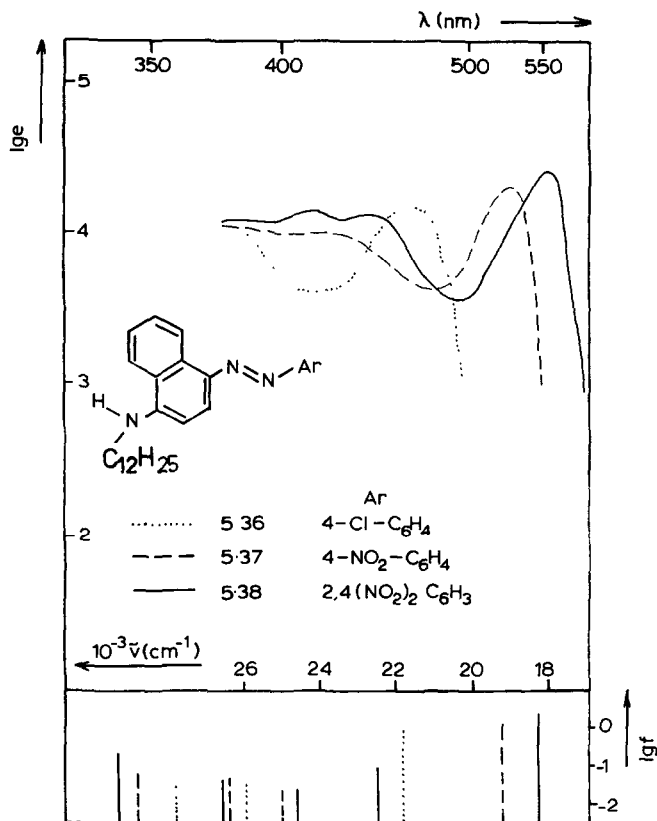


Fig. 1. Experimental spectral curves and calculated transition energies for the azo dyes 5.36, 5.37 and 5.38.

TABLE 9

Dichroic Ratio (D) and Order Parameter (S) of 1-Arylazo-4-naphthylamines **5** at their Absorption Maxima Measured in the Nematic Liquid Crystal Mixture CLF104A Containing 2 wt % of the Corresponding Dye at 25°C

Compound	λ_{\max} (nm) (in CLF104A)	D^a	S^b
5.10	591	9.09	0.71
5.11	585	9.09	0.71
5.12	590	9.29	0.73
5.13	589	9.09	0.71
5.14	572	9.09	0.71
5.36	585	9.29	0.73
5.37	595	9.29	0.73
5.38	602	9.29	0.73
5.39	600	9.29	0.73

^a Dichroic ratio $D = \epsilon_{\parallel}/\epsilon_{\perp}$.

^b Order parameter $S = (D - 1)/(D + 2)$.

crystalline systems. Due to their flat structure, which is similar to the structure of the liquid crystal medium used, the arylazonaphthylamines **5** show a high dichroic ratio (D) and a large order parameter (S). Therefore, the arylazonaphthylamines **5** can be used to enhance the contrast of nematic materials in liquid crystal displays.

The dichroic ratio (D) and order parameter (S) of several selected dyes are shown in Table 9.

Further details will be reported in a forthcoming paper.

3 EXPERIMENTAL

3.1 General

All melting points are uncorrected. The absorption spectra were measured in dimethylformamide at a concentration of 1×10^{-5} mol litre $^{-1}$ using an M40 UV/Vis spectrophotometer from VEB Carl Zeiss, Jena. The starting hydroxy-substituted arylazo compounds **1** and **2** were synthesized by the usual coupling reaction of the corresponding diazonium salt with the coupling component, according to the procedure described in Ref. 15, and recrystallized from methanol. All compounds gave satisfactory elemental analysis data.

The liquid crystalline compound CLF104A used for measuring the dichroic ratio (D) and the order parameter (S) was a gift from Mrs Dr Herzberg of the Werk für Fernsehelektronik Berlin enterprise.

The PPP calculations on the 1-arylazo-2- and -4-naphthylamines **5** and **7**, which are assumed, in accordance with the findings in Ref. 16, to exist solely in the tautomeric azo form, were performed by a standard procedure using

TABLE 10
Parameters for the PPP Calculation Accordingly to Ref. 23

Core		IP (ev)	EA (ev)	R_{cx} (pm)	B_{cx}/B_{cc}
Atom	Charge				
—C=	1	11.42	0.58	140	1.0
—N(CH ₃) ₂	2	21.22	8.24	140	1.0
—NH ₂	2	23.13	10.15	140	1.0
—N=	1	14.16	1.35	140	1.0
—OCH ₃	2	25.43	10.85	140	1.1
—OH	2	27.17	12.59	140	1.1
—O	1	17.28	2.70	122	1.2
—Cl	2	24.00	12.73	170	0.5
—Br	2	21.65	11.62	185	0.4

the semi-empirical parameters listed in Table 10 for the carbon and hetero-atoms contributing to the conjugated π -electron system of the compounds studied, and taking five occupied and five unoccupied orbitals for the CI-treatment into account.

3.2 Chloro-arylazo compounds 3 and 4

A mixture of 10 ml of equimolar amounts of POCl_3 and dimethylformamide (DMF) was added to a solution of 5 g of the appropriate hydroxy-arylazo compound **1** and **2** in 70 ml DMF at 0–5°C. The reaction mixture was heated on a steam bath and monitored by TLC until reaction was complete. The cooled solution was added to 50 ml methanol and 50 g ice. The products thus obtained were filtered and recrystallized from methanol.

3.3 Amino-arylazo compounds 5, 6 and 7

Method A

A solution of 3 g of the appropriate chloro-arylazo compound **3** or **4** in 50 ml of DMF was mixed with 20 ml of the amine and heated at about 100°C. The reaction was monitored by TLC. The reaction product was isolated by filtration after cooling and addition of acetic acid to the reaction mixture. The product was recrystallized from acetic acid.

Method B

The reaction was performed in a similar way to method A, but the mixture was heated with an excess of the appropriate amine with no further solvent, at the reflux temperature of the amine.

3.4 1-Arylamino-1*H*-naphth(1,2-*d*)imidazoles 9

The chloro-arylazo compound **4** (3 g) in 50 ml of DMF was mixed with 20 ml of the appropriate amine and the mixture was heated to about 100°C. The reaction was monitored by TLC. After cooling and adding 100 ml H_2O to the reaction mixture, the product was filtered and recrystallized from acetone.

3.5 Benzo(*b*)phenazines 10

The appropriate *N*-aryl-substituted 1-arylazo-2-naphthylamine **7** (3 g) was refluxed with conc. hydrochloric acid. The reaction solution was poured into methanol. The separated product was filtered, washed with water and purified by recrystallization from methanol.

3.6 5-Amino-3*H*-naphth(1,2-*d*)imidazoles 11

The appropriate chloro-substituted arylazo compound **3** or **4** (3 g) in 50 ml of DMF was mixed with 20 ml of the secondary amine and heated to about 100°C. The extent of the reaction was monitored by TLC. After complete reaction of the starting azo educt the reaction mixture was cooled and the product filtered after adding 100 ml H₂O to the reaction mixture. The product was recrystallized from DMF.

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