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PREPARATION OF NAPHTHOQUINONE IMINES AS NIR DYES

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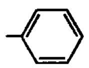
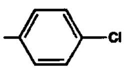
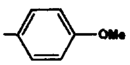
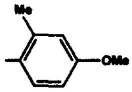
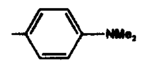
Abstract: N-Arylphthalimides can be converted to isoindoles by a two electron reduction and silylation. Cycloaddition with acetylenic dienophiles leads to naphthoquinonemonoimines, which show absorption maxima in the NIR region up to 800 nm.

Dyes with absorption maxima in the NIR range are of special interest today. Commercially available lasers emitting in this range (760-850 nm) open a wide potential of application for NIR dyes [1]. Organic dyes are used in photosemiconductors of laser printers [2] and as absorption media in laser filters [3]. Applications in optical data storage [4,5] and also in the photochemotherapy [6,7] are under investigation.

We could show that the electrochemical reduction and silylation of substituted phthalimides **1** leads to isoindoles [8,9]. By this procedure a variety of isoindoles with different substituents are available. Phthalimides accept an electron between -1.4 and -1.6 V (SCE) on cyclic voltammetry. A second equally reversible step corresponds to the formation of the dianion. Some representative data are given in table 1.

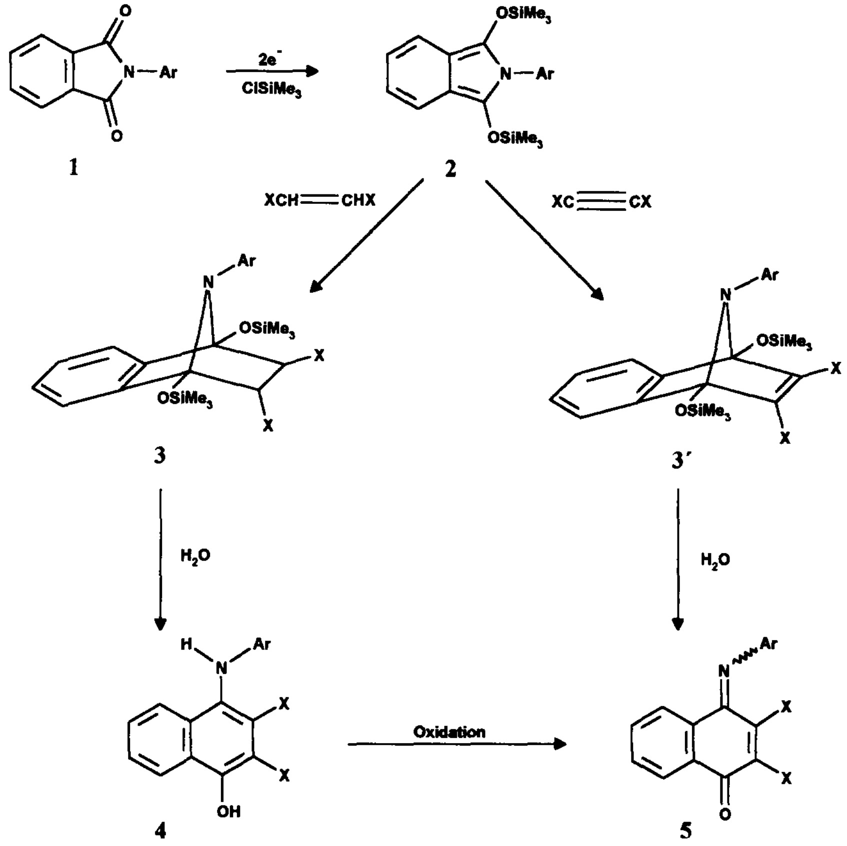
Table 1: Half wave potentials of phthalimides (CH_3CN, Pr_4NBF_4, vs SCE)

R =	$-CH_3$					
1	a	b	c	d	e	f
$E^1_{1/2}$ [V]	-1.39	-1.47	-1.39	-1.48	-1.50	-1.51
$E^2_{1/2}$ [V]	-2.10 (irr.)	-2.19	-2.10	-2.22	-2.30	-2.22

The electronic property of the N-aryl group has only a relatively small influence on the first reduction potential.

The preparative electrochemical reduction leads to yellow coloured solutions of **2**. The reaction of **2** with alkenes and alkines give the cycloadducts **3** and **3'**, leading to naphthaline and naphthoquinone derivatives upon aqueous work up.

Scheme 1:



In some cases the adduct **3** could be isolated by crystallization (X = CN, Ar = 4-chloro-phenyl, 4-methoxy-2-methyl-phenyl) and characterized by spectroscopic data. Otherwise the products **4** and **5** are isolated in a one step procedure in up to 65% yield. Quinone derivates **5** can also be obtained by the oxidation of **4** with suitable oxidizing agents like lead dioxide or tetraacetate and manganese dioxide.

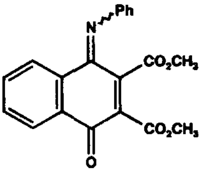
MO calculations show that the long wave absorption of **5** corresponds to an intramolecular charge transfer process [10]. Electron acceptor substituents in the quinone part and electron donors in the aryl group cause a shift of the absorption maxima to longer wavelengths.

A methoxy group in 2- and 4-position of the aryl group shifts the maximum by about 60 nm (see **6** and **7**,**9**,**10** and **11** in table 2). Planarity also plays an important role. Therefore the substitution of the ester group by a nitrile group causes a bathochromic shift of about 90 nm. This effect can be shown by comparing compounds **6** and **9** or **7** and **10**.

The steric requirements in the quinone imines lead to an enhanced rate of inversion of the N-aryl group. The NMR spectra are temperature dependent and show broad absorptions for the ester groups at room temperature. The energy barriers for the inversion lie between 18 and 19 kcal/mol.

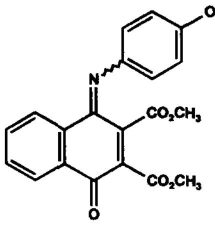
The long wave absorption maxima and intensities for some representative examples are given in table 2.

Table 2: Long wave absorptions of quinone imines **6** -**17** in chloroform (λ in nm, ε in $dm^3mol^{-1}cm^{-1}$)



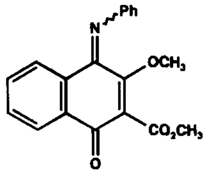
6

λ = 475 (ε = 3200), CH_3OH



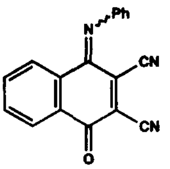
7

λ = 531 (ε = 6800)



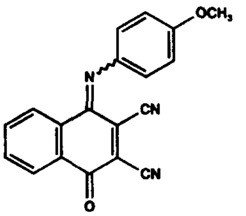
8

λ = 495 (ε = 3300), CH_3OH



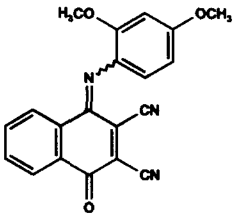
9

λ = 562 (ε = 2700), CH_3CN



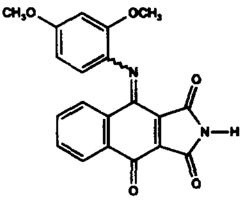
10

λ = 637 (ε = 7100)



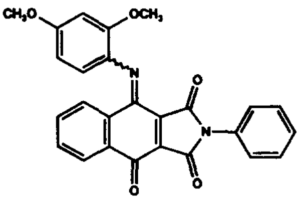
11

λ = 683 (ε = 5000)



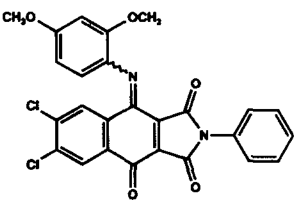
12

λ = 693 (ε = 4800)



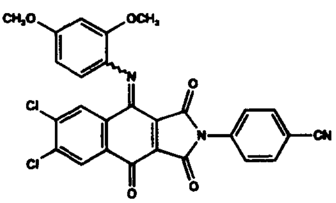
13

λ = 702 (ε = 4600)



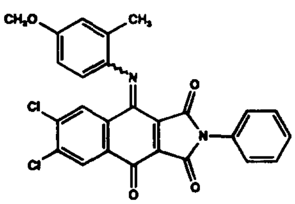
14

λ = 718 (ε = 5400)



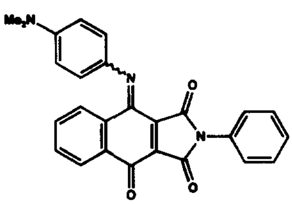
15

λ = 731 (ε = 7500)



16

λ = 698 (ε = 5800)



17

λ = 783 (ε = -*)

* only stable in solution

The reaction of isoindoles **2** with maleic imides leads upon oxidation to the quinone imines **12** - **17** with absorption maxima between 700 and 800 nm. For most of the compounds there exists only a small influence of the solvent upon the absorption maximum as shown in table 3.

Table 3: Influence of solvent on λ_{max} for **7**, **10** and **11**

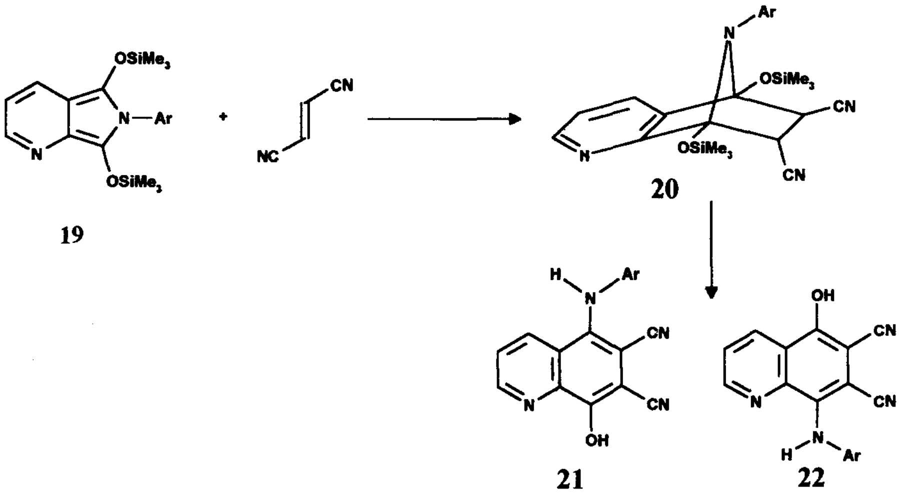
	n-Hexane	Acetonitrile	Chloroform	DMF
7	510 (7100)	523 (6800)	531 (6800)	530 (7400)
10	607 (3100)	622 (7000)	637 (7100)	605 (3900)
11	- *	668 (5600)	683 (5800)	670 (6200)

* not soluble

Calculations with semiempirical methods (AM1 [11], PM3 [12]) result in a helical structure as optimal geometry for the naphthoquinone imines. The calculated absorption maxima are at too short wavelengths in comparison with the experimental values [13].

Pyridine-2,3-dicarboximides can be converted to the orthoquinoid pyrido-pyrroles **19** in a similar way (scheme 2). Treatment of **19** with symmetrical dienophiles leads to isomeric quinoline derivatives **21** and **22**, whose constitution could be proved by NOE experiments [13]. The oxidation of **21** and **22** leads to dark green coloured solutions, but the isolation of crystalline products failed.

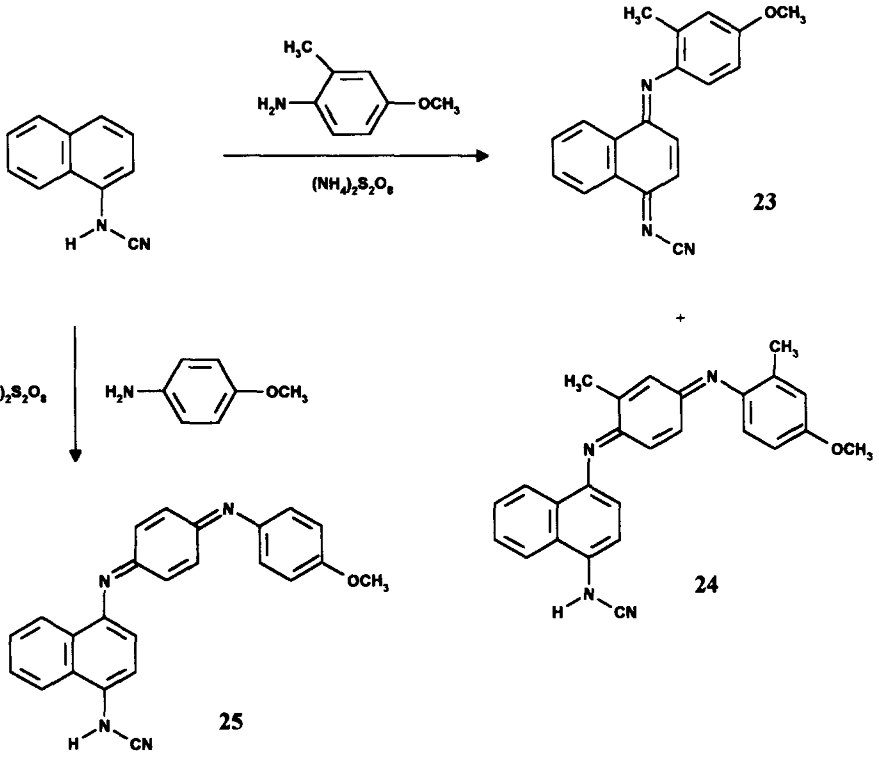
Scheme 2:



The reaction of **19** with dimethyl acetylene dicarboxylate also failed to give the expected quinone imine and dimethyl-5,8-dihydroxy-quinoline-6,7-dicarboxylate was isolated instead. The arylimino group is lost and the resulting quinone is reduced to its dihydro form during workup.

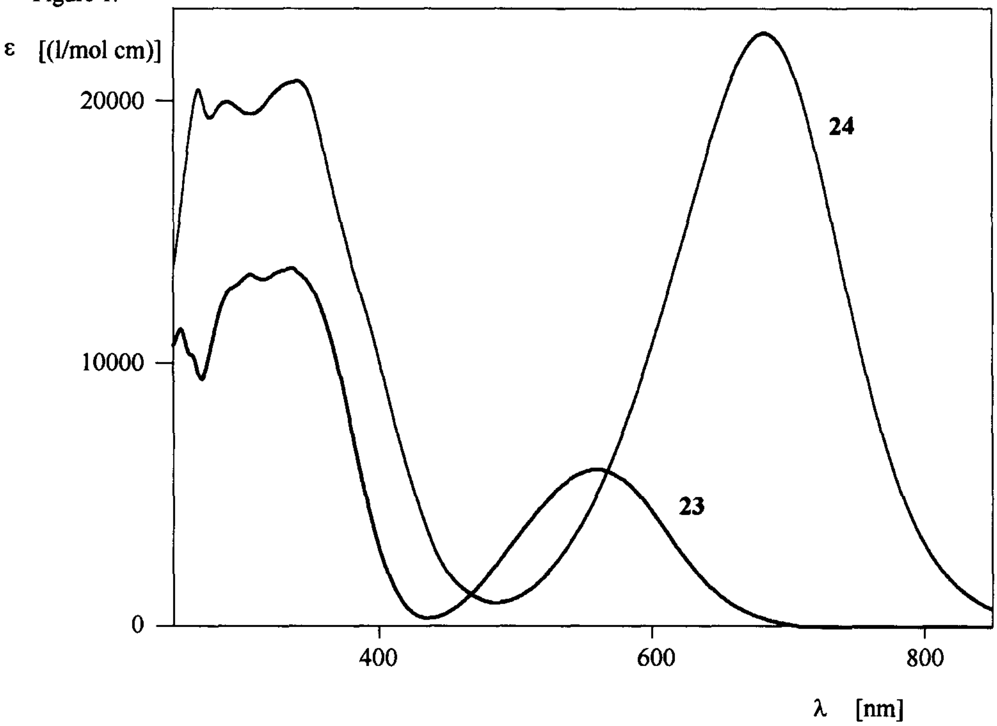
According to similar procedures described in the literature [14,15] 1-naphthylcyanamide was treated with 4-methoxy-2-methylaniline and ammonium peroxodisulfate as oxidizing agent. In addition to the expected adduct **23** we also isolated **24** which must have been formed by subsequent substitution of the 4-methoxy group by an aniline moiety. With p-methoxyaniline **25** is the only product isolated (scheme 3). **24** and **25** only exist in the tautomeric form with a benzoquinonediimine structure. The UV/VIS spectra of **23** and **24** are shown in figure 1.

Scheme 3:



Both compounds have long wave absorption maxima (**24**: 685 nm; **25**: 667 nm) with molar extinction coefficients exceeding 20 000 dm^{3}mol^{-1}cm^{-1}.

Figure 1:



Experimental

General:

^{1}H NMR Spectra were recorded at 400 MHz on a Bruker ARX 400, at 250 MHz on a Bruker WM 250 or at 60 MHz on a Varian ASS. EM 360 spectrometer using TMS δ_H 0.0 as an internal reference. All J values are given in Hz. ^{13}C NMR spectra were recorded on Bruker ARX 400 and WM 250. Absorption spectra were measured using a Hitachi U 2000 spectrophotometer. Mass spectra are obtained on a Finnigan MAT 112S/SS200 spectrometer. Melting points are not corrected. Elemental analyses: Heraeus CHN-Rapid instrument. For preparative electrochemistry a Bank Wenking ST 72 instrument is used as potentiostat and a Wenking SSI 70 as integrator.

Preparation of phthalimides 1

Phthalic anhydride and an equivalent amount of the aniline derivative are heated under reflux in acetic acid for 1-2 h . The solution was poured into water and the resulting precipitate is filtered off by suction and recrystallized.

N-Methyl-phthalimide (**1a**)
Yield 70%, mp. 133-134°C; IR (cm^{-1}) 1720 (C=O); 1600 (C=C);

N-Phenyl-phthalimide (**1b**)

Yield 90 %, mp. 205 - 206°C; IR (cm^{-1}) 1780, 1735, 1710 (C=O); 1615, 1600 (C=C); ^{1}H NMR (60 MHz, CDCl$_3$) 7.24 - 7.31 (m, 5H, Phenyl-H); 7.50 - 7.84 (m, 4H, Ar-H);

N-(4-Chlorphenyl)-phthalimide (**1c**)

Yield 81%, mp. 193-194°C; IR (cm^{-1}) 1780, 1740, 1710 (C=O); 1610 (C=C); ^{1}H NMR (60 MHz, CDCl$_3$) 7.42 - 7.48 (m, 4H, Ar-H); 7.76 - 7.99 (m, 4H, Ar-H);

N-(4-Methoxyphenyl)-phthalimide (**1d**)

Yield 84%, mp. 158-159°C; IR (cm^{-1}) 1770, 1755, 1740, 1710 (C=O); 1610, 1585 (C=C); ^1H NMR (60 MHz, $CDCl_3$) 3.83 (s, 3H, $-OC\underline{H}_3$); 6.90 - 7.48 (m, 4H, AA'BB'); 7.70 - 8.04 (m, 4H, Ar-$\underline{H}$);

N-(4-Methoxy-2-methylphenyl)-phthalimide (**1e**)

Yield 82%, mp. 142-143°C; IR (cm^{-1}) 2980, 2950, 2855 (CH sp^3); 1780, 1720, 1700 (C=O); 1615, 1585 (C=C); ^1H NMR (60 MHz, $CDCl_3$) 2.09 (s, 3H, $-C\underline{H}_3$), 3.97 (s, 3H, $-OC\underline{H}_3$), 6.60-7.09 (m, 3H, Ar-$\underline{H}$), 7.52-7.85 (m, 4H, Ar-$\underline{H}$);

N-(4-Dimethylaminophenyl)-phthalimide (**1f**)

Yield 74%, mp. 258-259°C; IR (cm^{-1}) 1775, 1695 (C=O); 1610 (C=C); ^1H NMR (60 MHz, $CDCl_3$) 2.95 (s, 6H, $-N(C\underline{H}_3)_2$), 6.54-6.78 (m, 2H, Ar-$\underline{H}$), 6.98-7.17 (m, 2H, Ar-$\underline{H}$), 7.53-7.83 (m, 4H, Ar-$\underline{H}$);

General procedure for preparative electrochemistry:

The preparative electrolysis was performed in a cylindrical divided cell with a mercury cathode and a platinum anode, using dry acetonitrile as solvent and tetraethylammonium chloride as supporting electrolyte. After the addition of 10 mmol of phthalimide and about 6 ml of chlorotrimethylsilane to the catholyte the electrolysis was run under controlled potential at 0°C.

At the end of the electrolysis 10 - 15 mmol of dienophile are added to the deep yellow coloured catholyte and stirred at room temperature. After 2 - 3 h the catholyte was poured into 400 ml aqueous $NaHCO_3$ and extracted with ether or methylene chloride. After evaporation of the solvent the crude product was purified by recrystallization or column chromatography (silica gel, methylene chloride).

Representative procedure for oxidation of dihydro form **4**:

Oxidation with $Pb(OAc)_4$

To a solution of the substrate (0.5 - 1 mmol) in chloroform or methylene chloride is added a 4-7 fold excess of $Pb(OAc)_4$. After 15 min the solution is filtered and the solvent is removed under reduced pressure. The crude product is recrystallized or purified by column chromatography.

N-(4-Chlorophenyl)-1,4-bis-(trimethylsilyloxy)-2,3-trans-dicyano-7-aza-benzo-norbornane (**3a**)

Yield 10%, mp. 166-167 °C; IR (cm^{-1}) 2270 (C≡N); ^1H NMR (250 MHz, $CDCl_3$) 0.15 (s, 9H, $-Si(C\underline{H}_3)_3$), 0.18 (s, 9H, $-Si(C\underline{H}_3)_3$), 2.92 (d, J_{AB}=4.45, 1H, $-C\underline{H}$), 3.62 (d, J_{AB}=4.45; 1H, $-C\underline{H}$), 6.78-6.84 (m, 2H, Ar-$\underline{H}$), 7.09-7.15 (m, 2H, Ar-$\underline{H}$), 7.27-7.49 (m, 3H, Ar-$\underline{H}$), 7.62-7.66 (m, 1H, Ar-$\underline{H}$); Found: C 58.57, H 5.70, N 8.49; $C_{24}H_{28}N_3O_2ClSi_2$ requires C 59.78, H 5.85, N 8.72%;

N-(4-Methoxy-2-methylphenyl)-1,4-bis-(trimethylsilyloxy)-2,3-trans- dicyano-7-aza-benzo-norbornane (**3b**)

Yield 13%, mp. 134-135 °C; IR (cm^{-1})2260 (C≡N), 1600 (C=C); ^1H NMR (250 MHz, $CDCl_3$) 0.07 (s, 9H, $-Si(C\underline{H}_3)_3$), 0.08 (s, 3H, $-Si(C\underline{H}_3)_3$), 2.43 (s, 3H, $-C\underline{H}_3$), 2.87 (d, J_{AB}=4.46, 1H, $-C\underline{H}$), 3.62 (d, J_{AB}=4.46; 1H, $-C\underline{H}$), 3.70 (s, 3H, $-OC\underline{H}_3$), 6.74 (d, 1H, Ar-$\underline{H}$), 7.33-7.41 (m, 2H, Ar-$\underline{H}$), 7.44-7.50 (m, 1H, Ar-$\underline{H}$), 7.60-7.62 (m, 1H, Ar-$\underline{H}$); Found: C 63.12, H 6.84, N 8.48; $C_{26}H_{33}N_3O_3Si_2$ requires C 63.51, H 6.76, N 8.54%;

2,3-Bis-(methoxycarbonyl)-1,4-naphthoquinone-1-phenyl-imine (**6**)

Yield 39%, mp. 109 - 110 °C; UV (CH_3OH) λ_{max} (ε $dm^3mol^{-1}cm^{-1}$) 244 (13 300), 275 (14 300), 336 (3 400), 475 (3 200); IR (cm^{-1}) 1750, 1735, 1650 (C=O); 1600 (C=C); ^1H NMR (80 MHz, $CDCl_3$) 3.15 (s, br, 2.3H, $-CO_2C\underline{H}_3$); 3.92 (s, br, 3.7H, $-CO_2C\underline{H}_3$); 6.85 - 8.49 (m, 9H, Ar-$\underline{H}$); ^{13}C NMR (62.89 MHz, DEPT, $CDCl_3$) 52.31, 52.99 ($CO_2\underline{C}H_3$); 117.34, 120.65, 125.27, 126.20, 127.67, 128.30, 128.99, 129.72 ($\underline{C}H$); 130.10 (quart. C); 131.36, 131.72, 132.55 ($\underline{C}H$); 133.32 (quart. C); 134.02 ($\underline{C}H$); 135.91, 139.05, 149.52, 149.68 (quart. C); 163.77, 163.89 (quart. C, $\underline{C}O_2CH_3$); 181.34 (quart.C, $\underline{C}$=O); Found: C 68.4, H 4.36, N 3.96; $C_{20}H_{15}NO_5$ requires C 68.76, H 4.33, N 4.01%;

2,3-Bis-(methoxycarbonyl)-1,4-naphthoquinone-1-(4-methoxyphenyl)-imine (**7**)

Yield 22%, mp. 108 °C; UV ($CHCl_3$) λ_{max} (ε $dm^3mol^{-1}cm^{-1}$) 253 (25 900), 273 (29 800), 531 (6 800); IR (cm^{-1}) 1745, 1730, 1655 (C=O); 1595, 1570 (C=C); ^1H NMR (250 MHz, $CDCl_3$) 3.23 und 3.90 (2s, 6H, -$CO_2C\underline{H}_3$); 3.82 (s, 3H, $OC\underline{H}_3$); 6.86-6.92 (m, 4H, AA'BB', Ar-$\underline{H}$); 7.62 - 7.68 (m, 1H, Ar-$\underline{H}$); 7.73-7.79 (m, 1H, Ar-$\underline{H}$); 8.13-8.17 (m, 1H, Ar-$\underline{H}$); 8.47 - 8.50 (m, 1H, Ar-$\underline{H}$); Found: C 66.26, H 4.59, N 3.64; $C_{21}H_{17}NO_6$ requires C 66.48, H 4.52, N 3.69%;

2-Methoxy-3-methoxycarbonyl-1,4-naphthoquinone-1-phenylimine (**8**)

Yield 41%, mp. 160 °C; UV (CH_3OH) λ_{max} (ε $dm^3mol^{-1}cm^{-1}$) 240 (12 600), 279 (18 300), 495 (3 300); IR (cm^{-1}) 1740, 1670, 1635 (C=O), 1590, 1565 (C=C); ^1H NMR (250 MHz, $CDCl_3$) 3.50 (s, 3H, -$OC\underline{H}_3$), 3.61 (s, 3H, -$OC\underline{H}_3$), 7.11-7.20 (m, 3H, Ar-$\underline{H}$), 7.30-7.37 (m, 2H, Ar-$\underline{H}$), 7.63-7.77 (m, 2H, Ar-$\underline{H}$), 7.94-7.98 (m, 1H, Ar-$\underline{H}$), 8.08-8.11 (m, 1H, Ar-$\underline{H}$); Found: C 69.84, H 4.96, N 4.30; $C_{19}H_{15}NO_4$ requires C 71.02, H 4.71, N 4.36%;

2,3-Dicyano-1,4-naphthoquinone-1-phenylimine (**9**)

Yield 14%, mp. 167-168°C; UV (CH_3CN) λ_{max} (ε $dm^3mol^{-1}cm^{-1}$) 277 (12 000), 342 (3 800), 562 (2 700); IR (cm^{-1}) 1670 (C=O), 1595 (C=C); m/z 283.1;

2,3-Dicyano-1,4-naphthoquinone-1-(4-methoxyphenyl)-imine (**10**)

Yield 19%, mp. 175-176°C; UV ($CHCl_3$) λ_{max} (ε $dm^3mol^{-1}cm^{-1}$) 281 (11 000), 338 (8 700), 637 (7 100); IR (cm^{-1}) 1670 (C=O), 1605, 1596, 1580 (C=C); ^1H NMR (250 MHz, $CDCl_3$) 3.90 (s, 3H, -$OC\underline{H}_3$), 7.00 (s (br), 4H, Ar-$\underline{H}$), 7.44-8.81 (m, 4H, Ar-$\underline{H}$); Found: C 71.09, H 3.40, N 12.91; $C_{19}H_{11}N_3O_2$ requires C 72.84, H 3.54, N 13.41%;

2,3-Dicyano-1,4-naphthoquinone-1-(2,4-dimethoxyphenyl)-imine (**11**)

Yield 19%, mp. 178-179°C; UV ($CHCl_3$) λ_{max} (ε $dm^3mol^{-1}cm^{-1}$) 288 (8 400), 340 (7 800), 683 (5 000); IR (cm^{-1}) 2955, 2850 (CH sp^3); 2240 (C≡N); 1640 (C=O); 1600, 1590 (C=C); 1550, 1510, 1455, 1310, 1280, 1250, 1215, 1120; ^1H NMR (250 MHz, $CDCl_3$) 3.71 (s, 3H, -$OC\underline{H}_3$), 3.90 (s, 3H, -$OC\underline{H}_3$), 6.50 (m, 1H, Ar-$\underline{H}$), 6.63-6.67 (m, 1H, Ar-$\underline{H}$), 7.03-7.09 (m, 1H, Ar-$\underline{H}$,), 7.62-7.71 (m, 2H, Ar-$\underline{H}$), 8.19-8.23 (m, 1H, Ar-$\underline{H}$); Found: C 68.06, H 3.81, N 11.88; $C_{20}H_{13}N_3O_3$ requires C 69.96, H 3.82, N 12.24%;

1,4-Naphthoquinone-1-(2,4-dimethoxyphenyl)-imine-2,3-dicarboximide (**12**)

Yield 25%, mp. 201°C; UV ($CHCl_3$) λ_{max} (ε $dm^3mol^{-1}cm^{-1}$) 335 (9 800), 693 (4 800); IR (cm^{-1}) 3280 (NH, Imide); 1720, 1655 (C=O); 1590, 1570 (C=C); ^1H NMR (250 MHz, $CDCl_3$) 3.79 (s, 3H, -$OC\underline{H}_3$), 3.87 (s, 3H, -$OC\underline{H}_3$), 6.50-6.55 (m, 1H, Ar-$\underline{H}$), 6.57-6.58 (m, 1H, Ar-$\underline{H}$), 6.90-6.93 (m, 1H, Ar-$\underline{H}$), 7.62-7.75 (m, 2H, Ar-$\underline{H}$), 8.20-8.25 (m, 1H, Ar-$\underline{H}$), 8.55-8.58 (m, 1H, Ar-$\underline{H}$); Found: C 64.26, H 4.40, N 7.21; $C_{20}H_{14}N_2O_5$ requires C 66.30, H 3.89, N 7.73%;

1,4-Naphthoquinone-1-(2,4-dimethoxyphenyl)-imine-2,3-dicarboxylic-acid-N-phenyl-imide (**13**)

Yield 28%, mp. 226-227°C; UV ($CHCl_3$) λ_{max} (ε $dm^3mol^{-1}cm^{-1}$) 362 (10 900), 702 (4 600); IR (cm^{-1}) 1720, 1635 (C=O); 1600, 1590, 1580 (C=C); ^1H NMR (250 MHz, $CDCl_3$) 3.79 (s, 3H, -$OC\underline{H}_3$), 3.86 (s, 3H, -$OC\underline{H}_3$), 6.48-6.49 (m, 1H, Ar-$\underline{H}$), 6.54-6.58 (m, 1H, Ar-$\underline{H}$), 6.95-6.99 (m, 1H, Ar-$\underline{H}$), 7.22-7.26 (m, 1H, Ar-$\underline{H}$), 7.32-7.46 (m, 4H, Ar-$\underline{H}$), 7.63-7.76 (m, 2H, Ar-$\underline{H}$), 8.23-8.26 (m, 1H, Ar-$\underline{H}$), 8.56-8.58 (m, 1H, Ar-$\underline{H}$); Found: C 69.41, H 4.33, N 6.01; $C_{26}H_{18}N_2O_5$ requires C 71.23, H 4.14, N 6.39%;

6,7-Dichloro-1,4-naphthoquinone-1-(2,4-dimethoxyphenyl)-imine-2,3-dicarboxylic-acid-N-phenyl-imide (**14**)

Yield 15%, mp. 229-230°C; UV ($CHCl_3$) λ_{max} (ε $dm^3mol^{-1}cm^{-1}$) 411 (14 100), 718 (5 400); IR (cm^{-1}) 1770, 1720, 1635 (C=O); 1605, 1570 (C=C); ^1H NMR (250 MHz, $CDCl_3$) 3.78 (s, 3H, -OCH_3), 3.87 (s, 3H, -OCH_3), 6.45-6.46 (m, 1H, Ar-H), 6.57-6.61 (m, 1H, Ar-H), 7.02-7.06 (m, 1H, Ar-H), 7.22-7.25 (m, 2H, Ar-H), 7.33-7.47 (m, 3H, Ar-H), 8.29 (s, 1H, Ar-H), 8.62 (s, 1H, Ar-H); Found: C 59.65, H 3.19, N 5.27; $C_{26}H_{16}N_2O_5Cl_2$ requires C 61.55, H 3.19, N 5.52%;

6,7-Dichloro-1,4-naphthoquinone-1-(2,4-dimethoxyphenyl)-imine-2,3-dicarboxylic-acid-N-(4-cyano-phenyl)-imide (**15**)

Yield 10%, mp. 213-215°C; UV ($CHCl_3$) λ_{max} (ε $dm^3mol^{-1}cm^{-1}$) 731 (7 500); IR (cm^{-1}) 2240 (C≡N); 1725, 1645 (C=O); 1605, 1585 (C=C); ^1H NMR (400 MHz, $CDCl_3$) 3.78 (s, 3H, -OCH_3), 3.89 (s, 3H, -OCH_3), 6.48 (d, 1H, Ar-H), 6.61 (dd, 1H, Ar-H), 7.03 (d, 1H, Ar-H), 7.46 (m, 2H, Ar-H, AA'BB'), 7.73 (m, 2H, Ar-H, AA'BB'), 8.30 (s, 1H, Ar-H), 8.62 (s, 1H, Ar-H);

6,7-Dichloro-1,4-naphthoquinone-1-(4-methoxy-2-methylphenyl)-imine-2,3-dicarboxylic-acid-N-phenyl-imide (**16**)

Yield 15%, mp. 203-205°C; UV ($CHCl_3$) λ_{max} (ε $dm^3mol^{-1}cm^{-1}$) 340 (6 300), 368 (7 100), 698 (5 800); IR (cm^{-1}) 1720, 1645 (C=O); 1605, 1585, 1575 (C=C); ^1H NMR (250 MHz, $CDCl_3$) 2.49 (s, 3H, -CH_3), 3.78 (s, 3H, -OCH_3), 6.45-6.49 (m, 1H, Ar-H), 6.62-6.69 (m, 1H, Ar-H), 6.94-6.96 (m, 1H, Ar-H), 7.15-7.19 (m, 2H, Ar-H), 7.29-7.48 (m, 3H, Ar-H), 8.30 (s, 1H, Ar-H), 8.66 (s, 1H, Ar-H); Found: C 61.71, H 3.78, N 5.54; $C_{26}H_{16}N_2O_4Cl_2$ requires C 63.67, H 3.29, N 5.71%;

6,7-Dicyano-8-hydroxy-5-(4-methoxyphenylamino)-quinoline (**21a**)

Yield 7%, mp. 208-210°C; IR (cm^{-1}) 3450-3050 (OH); 2240, 2220 (C≡N); ^1H NMR (250 MHz, DMSO-d_6) 3.76 (s, 3H, -OCH_3); 6.89-6.93 (m, 2H, Ar-H, AA'BB'); 7.19-7.23 (m, 2H, Ar-H, AA'BB'); 7.86-7.92 (m, 1H, Ar-H); 8.70-8.74 (m, 1H, Ar-H); 8.98 (s, 1H, -NH); 9.07-9.10 (m, 1H, Ar-H); ca. 11.55 (br, 1H, -OH);

6,7-Dicyano-5-hydroxy-8-(4-methoxy-2-methylphenylamino)-quinoline (**21b**)

Yield 19%, mp. 219-221 °C; IR (cm^{-1}) 3500-3100 (OH); 3240 (NH); 2220 (C≡N); 1610, 1580 (C=C); ^1H NMR (400 MHz, $CDCl_3$) 2.42 (s, 3H, -CH_3), 3.77 (s, 3H, -OCH_3), 4.11 (br, 1H, -OH), 5.88 (s, 1H, -NH), 6.46-6.48 (m, 1H, Ar-H), 6.53-6.56 (m, 1H, Ar-H), 6.84-6.86 (m, 1H, Ar-H), 7.45-7.48 (m, 1H, Ar-H), 8.00-8.03 (m, 1H, Ar-H), 8.91-8.93 (m, 1H, Ar-H); Found: C 67.29, H 4.06, N 16.34; $C_{19}H_{14}N_4O_2$ requires C 69.08, H 4.27, N 16.96%;

6,7-Dicyano-5-hydroxy- 8-(4-methoxyphenylamino)-quinoline (**22a**)
Yield 30%, mp. 222-224 °C; IR (cm^{-1}) 3500-3000 (OH); 3300 (NH); 2215, 2195 (C≡N); ^1H NMR (250 MHz, DMSO-d_6) 3.69 (s, 3H, -OCH_3); 6.80 (s, 4H, Ar-H, AA'BB'); 7.79-7.84 (m, 1H, Ar-H); 8.51 (s, 1H, -NH); 8.51-8.55 (m, 1H, Ar-H); 9.10-9.12 (m, 1H, Ar-H); Found: C 66.79, H 4.11, N 16.97; $C_{18}H_{12}N_4O_2$ requires C 68.35, H 3.82, N 17.71%;

General procedure for the preparation of the substituted bis-imino dyes 23 - 25
To an aq. KOH solution of naphthylcyanamide at 5°C were added dropwise aq. solutions of 4-methoxy-aniline and an oxidizing agent (ammonium peroxodisulfate e.g.). After stirring the mixture for 30 min, the products were extracted with chloroform, the solvent was evaporated and the crude product was chromatographed on silica gel.

N-Cyano-N'-(4-methoxy-2-methylphenyl)-1,4-naphthoquinonediimine (**23**)

Yield 3%, mp.: 179-181 °C; UV ($CHCl_3$) λ_{max} (ε $dm^3mol^{-1}cm^{-1}$) 255 (11 100), 289 (12 800), 335 (13 800), 564 (6 200); IR (cm^{-1})2190 ($C{\equiv}N$), 1605 ($C{=}C$); ^1H NMR (250 MHz, $CDCl_3$) 2.30 (s, 3H, $-C\underline{H}_3$), 3.85 (s, 3H, $-OC\underline{H}_3$), 6.59 (d, 1H, Ar-$\underline{H}$), 6.76-6.81 (d, 1H, Ar-$\underline{H}$), 6.90 (d, 1H, Ar-$\underline{H}$), 7.25 (d, 1H, C-$\underline{H}$, J_{AB} = 10.2), 7.43 (d, 1H, C-$\underline{H}$, J_{AB} = 10.2), 7.64-7.70 (m, 1H, Ar-$\underline{H}$), 7.77-7.83 (m, 1H, Ar-$\underline{H}$), 8.36-8.39 (m, 1H, Ar-$\underline{H}$), 8.58-8.61 (m, 1H, Ar-$\underline{H}$); ^{13}C NMR (100.61 MHz, $CDCl_3$, DEPT) 18.59 ($-\underline{C}H_3$), 55.51 ($-O\underline{C}H_3$), 111.17 ($\underline{C}H$), 114.68 ($\underline{C}{\equiv}N$), 116.78, 121.34, 125.31, 125.59, 127.03, 128.76 (quart. C), 130.96, 133.85 ($\underline{C}H$), 134.04, 134.52, 141.79, 152.65, 159.01, 175.58 (quart. C); Found: C 75.05, H 5.29, N 13.53; $C_{19}H_{15}N_3O$ requires C 75.73, H 5.02, N 13.94%; m/z 301.2;

N-(4-Cyanamino-1-naphthyl)-N'-(4-methoxy-2-methylphenyl)-2-methyl-1,4-benzoquinonediimine (**24**)

Yield 2%, mp.: 180-182°C; UV ($CHCl_3$) λ_{max} (ε $dm^3mol^{-1}cm^{-1}$) 286 (20 600), 341 (20 800), 685 (22 600); IR (cm^{-1}) 3370 (NH); 2180 ($C{\equiv}N$); 1585 ($C{=}C$); ^1H NMR (250 MHz, $CDCl_3$) 2.26 (s, 3H, $-C\underline{H}_3$), 2.33 (s, 3H, $-C\underline{H}_3$), 3.82 (s, 3H, $-OC\underline{H}_3$), 5.49 (s, 1H, -NH), 6.55-6.60 (m, 2H, $=C-\underline{H}$), 6.70-6.71 (m, 1H, $=C-\underline{H}$), 6.76-6.84 (m, 2H, Ar-$\underline{H}$), 7.19 (m, 1H, Ar-$\underline{H}$), 7.35 (d, 1H, Ar-$\underline{H}$, J_{AB}=10.2), 7.43 (d, 1H, Ar-$\underline{H}$, J_{AB}=10.2), 7.59-7.66 (m, 1H, Ar-$\underline{H}$), 7.73-7.80 (m, 1H, Ar-$\underline{H}$), 8.35-8.38 (m, 1H, Ar-$\underline{H}$), 8.57-8.61 (m, 1H, Ar-$\underline{H}$); Found: C 75.18, H 5.53, N 13.51; $C_{26}H_{22}N_4O$ requires C 76.82, H 5.46, N 13.79%;

N-(4-Cyanamino-1-naphthyl)-N'-(4-methoxyphenyl)-1,4-benzoquinonediimine (**25**)

Yield 3%, mp. 168-169°C; UV ($CHCl_3$) λ_{max} (ε $dm^3mol^{-1}cm^{-1}$) 268 (18 400), 330 (20 700), 667 (18 200); IR (cm^{-1}) 3370 (NH); 2180 ($C{\equiv}N$); 1585 ($C{=}C$); ^1H NMR (250 MHz, $CDCl_3$) 3.82 (s, 3H, $-OC\underline{H}_3$), 5.84 (s, 1H, -NH), 6.89-6.95 (m, 2H, Ar-$\underline{H}$), 6.97 (m, 4H, Ar-$\underline{H}$), 7.15 (m, 2H, Ar-$\underline{H}$), 7.38 (d, 1H, Ar-$\underline{H}$, J_{AB}=10.2), 7.44 (d, 1H, Ar-$\underline{H}$, J_{AB}=10.2), 7.61-7.67 (m, 1H, Ar-$\underline{H}$), 7.72-7.80 (m, 1H, Ar-$\underline{H}$), 8.35-8.38 (m, 1H, Ar-$\underline{H}$), 8.54-8.57 (m, 1H, Ar-$\underline{H}$); Found: C 75.99, H 4.61, N 14.41; $C_{24}H_{18}N_4O$ requires C 76.17, H 4.79, N 14.81%;

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