Novel Chromophoric Heterocycles Based on Maleimide and Naphthoquinone

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1-Phenyl-3,4-dichloromaleimide, 1-*n*-propyl-3-bromomaleimide, and 2,3-dichloro-1,4-naphthoquinone have been condensed with various mono- and bis-nucleophiles to yield a range of novel dyes and pigments. Their visible absorption spectra are discussed.

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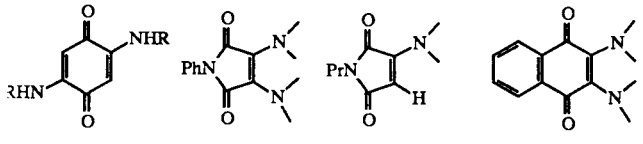
The "merostabilization" [1] of free radicals has been experimentally established in our [2] and other laboratories [3-5], and recent theoretical calculations have suggested significant merostabilization in polar media [6]. The intense color of indigo has been attributed [7-8] to merostabilization in the excited state and the strong color of other classes of compounds, for example bisaminoquinones **1** [9], can be similarly explained. Recently, we have used the theory of merostabilization of the excited state to search new areas of dyestuff chemistry including azaindigoes [10], bisalkylidinepiperazinediones [11], and alkylideneindoxyls [12]. The present work represents a further extension of this research to derivatives of maleimide and naphthoquinone of partial structures **2** to **4**.

Block 1



1 **2** **3** **4**

3,4-Dichloro-*N*-phenylmaleimide **5**, readily available [13] by treating *N*-phenylmaleimide with thionyl chloride in the presence of pyridine, has previously been reacted with alcohols, phenols and amines [13-15]. We have now investigated analogous reactions with other nucleophiles (Scheme 1 and Table 1). Pyrazole, 4-pyridone, and 4-dimethylaminopyridine gave the expected 3,4-disubstituted maleimide derivatives **6** to **8** in good yields. With imidazole in absolute ethanol the mixed product **10** was obtained, however, 3,4-bis-(1-imidazolyl)-*N*-phenylmaleimide **9** was produced (30%) when the reaction was carried out in dry acetonitrile. Phenylhydrazine gave the orange product **11**. The ^1H and ^{13}C nmr spectra and elemental analyses of compounds **6** to **11** comfirmed the structures assigned (Tables 2-4).

Scheme 1

5

6 R = R' = 1-pyrazolyl
7 R = R' = 1-(4-pyridone)
8 R = R' = 1-(4-dimethylaminopyridyl)
9 R = R' = 1-imidazoyl
10 R = 1-imidazoyl, R' = OCH_2CH_3
11 R = R' = PhNHNH

Attempts to cyclize the *N*-phenylmaleimide derivatives **6, 7, 9** and **11** failed. We therefore turned to the use of bis-nucleophiles to obtain such cyclized derivatives (Scheme 2). Dichloro-*N*-phenylmaleimide **5** reacted in absolute ethanol with *o*-aminophenol at 20° to give the deep yellow monosubstituted product 3-(2-hydroxyanilino)-4-chloro-*N*-phenylmaleimide **12** (68%). However, the reaction of **5** with *o*-aminothiophenol afforded the desired brown cyclized product **13**. Interestingly, reaction of **5** with *o*-phenylenediamine gave the yellow pyrroloquinoxaline **14** (76%) in a cyclization of a type different to that for *o*-aminothiophenol. Previously, such pyrroloquinoxaline and pyrrolobenzothiazine ring systems have been prepared by the reactions of amines with bisbromomethylquinoxaline or -benzothiazine derivatives derived from *o*-phenylenediamine or aminothiophenol (for example, see ref 16). The structure assignment for **14** was supported by elemental analysis and by the ir spectrum. We consider tautomeric structure **14a** as most likely, but **14b** cannot presently be excluded. Compound **5** reacted with dithiooxamide in dimethylformamide and triethylamine at 25° to give the black dyestuff **15** (70%). The preparative conditions and analyses for compounds **12-15** are summarized in Tables 1 and 2.

Propylamine and maleic anhydride in xylene yield *N*-propylmaleimide (21%), brominated in carbon tetrachloride to the dibromoderivative (84%) which was converted into 3-bromo-*N*-propylmaleimide **16** (90%) by eliminating hydrogen bromide with sodium acetate [17-18]. The ^1H nmr spectrum of **16** shows an olefin proton singlet and the typical $CH_3CH_2CH_2$ pattern. The ^{13}C nmr spectrum disclosed two carbonyl signals, two sp^2 carbons and the propyl group pattern. Elemental analysis confirmed the structure.

Scheme 2

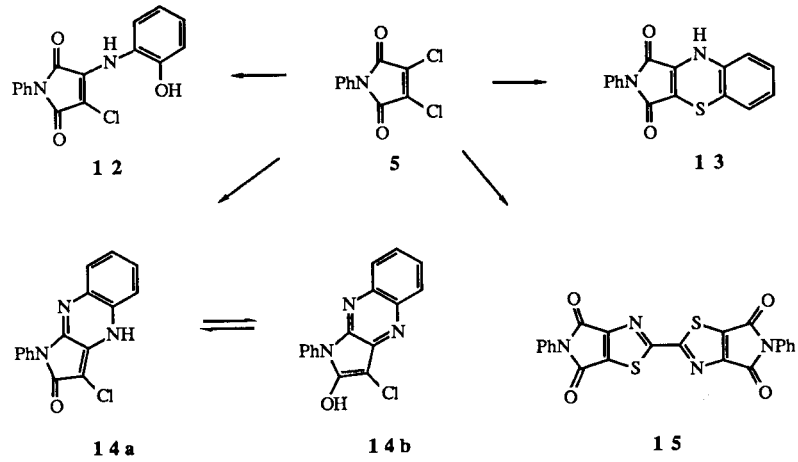


Table 1

Preparation of *N*-Phenylmaleimide Derivatives

Compounds	Nucleophile nature	ratio [a]	yield %	Crystal form [b]	Solvent Heating nature	ml	time hours	temp °C
6	pyrazole	1:5	64	yellow needles	EtOH	15	48	60
7	4-pyridone	1:4	60	red plates	CH_3CN	10	48	65
8	DMAP [c]	1:4	64	yellow micro	CH_3CN	15	2	60
9	imidazole	1:5	30	yellow needles	CH_3CN	15	10	60
10	imidazole	1:5	45	yellow needles	EtOH	15	15	62
11	$PhNHNH_2$	1:5	91	orange needles	EtOH	100	4	50
12	*o*-aminophenol	1:4	68	yellow needles	EtOH	70	16	40
13	*o*-$HSC_6H_4NH_2$	1:1	77	brown micro	EtOH	80	15	reflux
14	*o*-$C_6H_4(NH_2)_2$	1:1	76	yellow micro	EtOH	60	10	reflux
15	dithiooxamide	2:1	70	black micro	DMF	30	10	60

[a] The ratio of 3,4-dichloro-*N*-phenylmaleimide to nucleophile. [b] Micro means microcrystals. [c] *p*-Dimethylaminopyridine.

Table 2

Analytical Data for *N*-Phenylmaleimide Derivatives **6-15**

Compounds	Mp (°C)	Calcd. C	H	N	Formula	Found C	H	N
6	154-155	62.94	3.63	22.94	$C_{16}H_{11}N_5O_2$	62.92	3.56	22.83
7	249-251	66.85	3.65	11.69	$C_{20}H_{13}N_3O_4$	66.45	3.67	11.47
9	160-161	62.94	3.63	22.94	$C_{16}H_{11}N_5O_2$	62.74	3.63	22.82
10	108-109	63.60	4.63	14.83	$C_{15}H_{13}N_3O_3$	63.26	4.71	14.72
11	259-260	68.56	4.97	18.17	$C_{22}H_{19}N_5O_2$	68.35	4.69	18.25
12	205-206	61.06	3.52	8.90	$C_{16}H_{11}ClN_2O_3$	61.28	3.49	8.79
13	270-272	65.31	3.40	9.54	$C_{16}H_{10}SN_2O_2$	65.61	3.26	9.22
14	› 300	64.97	3.38	14.21	$C_{16}H_{10}ClN_3O$	65.03	3.37	14.04
15	227-230	57.64	2.18	12.23	$C_{22}H_{12}N_4O_4S_2$	57.57	2.19	12.27

Table 3

Spectral Data of *N*-Phenylmaleimide Derivatives

Compounds	IR (bromoform)	^{1}H NMR (dimethyl suloxide-d_6)
6	1693, 1597, 1498	8.21 (d, 2H, PyH), 7.77 (d, 2H, PyH), 7.39-7.22 (m, 5H), 6.43 (m, 2H).
7	1760, 1700, 1630 1590, 1490, 1290	8.90 (d, 4H, PyH), 7.3-7.4 (m, 5H), 7.26 (d, 4H, J = 7.5 Hz, PyH).
8	1787, 1720, 1695 1645, 1580, 1298	8.17 (d, 4H, PyH), 7.1-7.9 (m, 5H), 6.96 (d, 4H, PyH), 2.03 (s, 12H).
9	1730, 1690, 1600 1500, 1290.	8.02 (s, 2H), 7.42-7.45 (m, 5H), 7.15 (d, 4H, Im-H).
10	1688, 1600, 1500 1322, 1245.	8.37 (1H, t, J = 0.9 Hz), 7.75 (1H, t, Im-H), 7.29-7.45 (m, 5H, Ph-H), 7.17 (dd, 1H, ImH), 4.78 (q, 2H), 1.46 (t, 3H, CH_3).
11	3270, 1750, 1690 1600, 1580, 1230	12.01 (s, 2H, enamine NH), 11.54 (s, 2H, NH), 7.05-7.60 (m, 5H, AR-H).

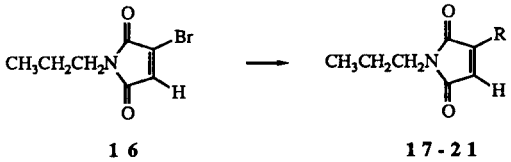
Table 4

^{13}C NMR Spectra of *N*-Phenylmaleimide Derivatives

Compound No.	C=O	CH=	Phenyl group				Substituent			
6	163.8	143.6	130.3	128.3	126.1	122.5	132.6	129.1	108.4	
7	163.0	142.7	132.3	128.3	126.4	121.6	168.3	114.2	100.2	
8	163.4	143.9	130.8	128.9	126.8	120.8	136.8	128.9	124.3	37.7
9	163.6	137.3	130.0	128.9	126.1	121.0	131.6	129.5	119.9	
10	163.3	139.9	130.2	129.5	126.1	117.8	129.0 15.6	128.0	119.7	69.7
11	161.8	141.9	131.1	128.3	125.1	123.5	129.6 114.5	128.8	127.0	124.4

3-Bromo-*N*-propylmaleimide **16** reacted with various nitrogen nucleophiles (Scheme 3 and Table 5): primary amines (allylamine giving **17**, phenylamine **18**, benzylamine **19**, and *p*-aminophenol **20**), heterocyclic compounds (pyrazole giving **21**, 1,2,4-triazole **22**, phenylpyrazolone **25**, and benzotriazole **23**), and phenylhydrazine giving **24**. Derivatives **17-25** were characterized analytically (Table 6) and by their ^{1}H (Table 7) and ^{13}C nmr spectra (Table 8). The reaction of 3-bromo-*N*-propylmaleimide **16** with *o*-phenylenediamine afforded an orange product which was assigned the cyclized structure **26** based on its analysis and spectra.

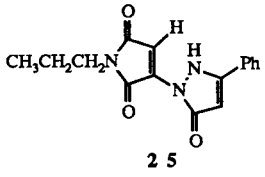
Scheme 3



16 **17-21**

17 R = CH_2=$CHCH_2NH$
18 R = PhNH
19 R = $PhCH_2NH$
20 R = *p*-HOC_6H_4NH

21 R = 1-pyrazolyl
22 R = 1-triazolyl
23 R = 1-benzotriazolyl
24 R = PhNHNH



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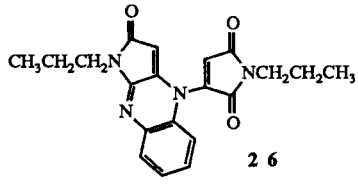

26

2,3-Dihalo-1,4-naphthoquinones undergo nucleophilic substitution with a variety of amines, thiols and alcohols to give 2,3-disubstituted naphthoquinones [15,19]. We now describe the synthesis of some new derivatives from 2,3-dichloro-1,4-naphthoquinone **27** and a variety of nucleophiles (Scheme 5). Pyrazole in ethanol afforded 2,3-dipyrazole-1,4-naphthoquinone **28**, hydrolyzed by sodium hydroxide to deep orange 2-hydro-3-(1-pyrazolyl)-1,4-naphthoquinone **29** as determined from ^{1}H and ^{13}C nmr and confirmed by elemental analysis and the mass spectrum. Pyridine replaces one of the chlorine atoms of **27** forming a monoadduct, which is easily hydrolyzed to zwitterion **30** [20]. We find that 4-dimethylaminopyridine similarly forms the red zwitterion **31**. 4-Pyridone as the nucleophile gave orange 2-(4-pyridone-1-yl)-3-hydro-1,4-naphthoquinone **32** as shown by the mass and ^{1}H nmr spectra and analysis.

Scheme 4

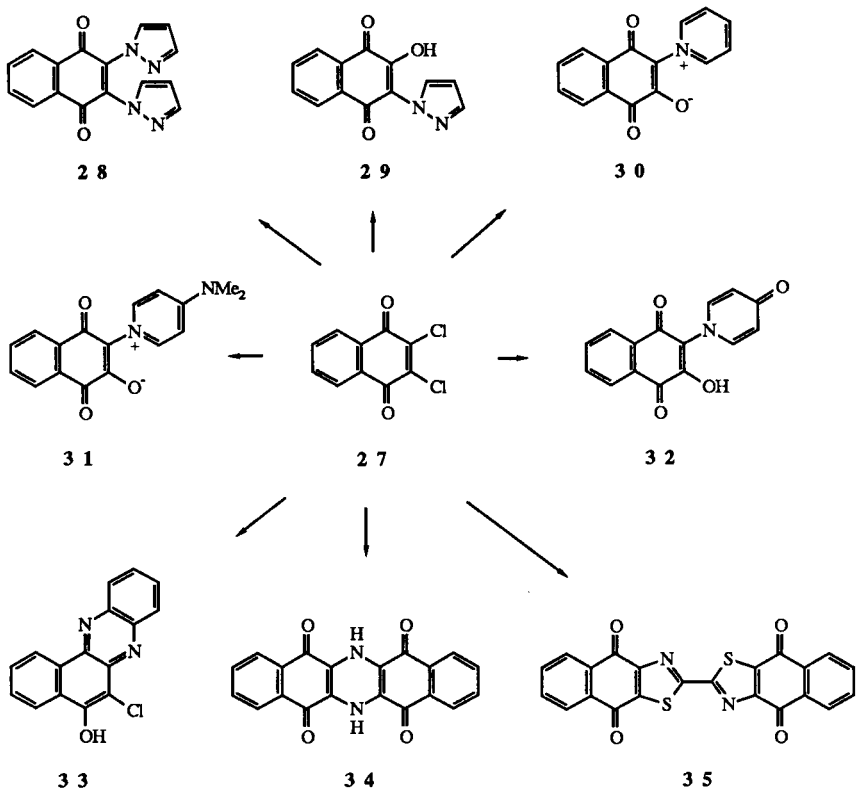

Table 5

Preparation of Mono-substituted*N*-propylmaleimide

Compound No.	Nucleophile [a]	Heating Time hours	Heating temp °C	Yield %	Crystal form	Mp (°C)
17	allylamine	3h	25	61	yellow needles	65-67
18	aniline	4h	reflux	58	yellow needles	143-145
19	benzylamine	3h	reflux	52	yellow needles	108-110
20	*p*-aminophenol	4h	25	51	yellow needles	190-192
21	pyrazole	48h	65	59	white needles	75-77
22	1,2,4-triazole	72h	reflux	46	pale needles	80-82
23	[b]	10h	25	55	brown microcrystals	122-124
24	benzotriazole	72h	reflux	44	pale needles	129-131
25	PhNHNH2	4h	reflux	61	orange needles	188-190
26	*o*-$C_6H_4(NH_2)_2$	8h	reflux	60	orange needles	202-204

[a] The ratio of 3-bromo-*N*-propylmaleimide to nucleophile is 1:2. [b] The nulceophile is 3-phenylpyrazolidin-5-one.

Table 6

Analytical Data for Mono-substituted-*N*-propylmaleimides

Compound No.	Calcd. C	Calcd. H	Calcd. N	Formula	Found C	Found H	Found N
17	61.86	7.22	14.23	$C_{10}H_{14}N_2O_2$	61.95	7.41	13.95
18	67.83	6.09	12.17	$C_{13}H_{14}N_2O_2$	67.82	6.31	12.07
19	68.85	6.56	11.48	$C_{14}H_{16}N_2O_2$	68.63	6.76	11.23
20	63.41	5.69	11.38	$C_{13}H_{14}N_2O_3$	63.11	5.87	11.25
21	58.54	5.37	20.49	$C_{10}H_{11}N_3O_2$	58.21	5.40	20.31
22	52.43	4.87	27.18	$C_9H_{10}N_4O_2$	52.34	4.92	27.20
23	64.65	5.05	14.13	$C_{16}H_{15}N_3O_3$	64.29	5.20	13.78
24	60.94	4.69	21.46	$C_{13}H_{12}N_4O_2$	61.26	4.69	21.20
25	63.67	6.12	17.14	$C_{13}H_{15}N_3O_2$	63.63	6.29	17.14
26	65.93	5.49	15.38	$C_{20}H_{20}N_4O_3$	66.30	5.59	15.22

Table 7

Spectral Data for Mono-substituted-*N*-propylmaleimides

Compound No.	UV/Vis (δ)	IR ($CHBr_3$)	Heating $CH_3CH_2CH_2$	=CH (s)	Substituent
17	364 (3240)	3400, 1700, 1650, 1500	0.85, 1.60, 3.45	5.75	6.3 (br s, NH), 5.1-5.5 (m, $=CH_2$), 5.7 (m, CH=), 3.85 (CH_2N)
18	389 (7690)	3340, 1700, 1630, 1590	0.85, 1.40, 3.45	5.5	9.6 (s, NH), 7.3 (m)
19	364 (3010)	3390, 1700, 1640, 1500	0.95, 1.55, 3.45	4.85	8.95 (br s, NH), 7.55 (s, 5H), 4.45 ($NHCH_2$)
20	400(8360)	3300, 1690, 1630, 1510	0.75, 1.50, 3.40	5.80	9.62 (2H, NH, OH), 7.32 (d, 2H, ArH), 6.85 (d, 2H, ArH)
21	344 (3500)	1710, 1640, 1530	0.90, 1.65, 3.50	8.00	8.8 (d, 1H), 6.6 (t, 2H)
22	326 (2920)	1720, 1650, 1510, 1440	0.85, 1.65, 3.55	6.70	9.35 (s, 1H), 8.20 (s, 1H)
23	392 (2000)		0.85, 1.50, 3.33	[a]	7.1-7.5 (m, 8H)
24	327 (1900)	1710, 1630	0.95, 1.70, 3.80	7.00	8.5-7.5 (m)
25	395 (29200)	3280, 1700, 1600, 1490	0.85, 1.60, 3.50	[a]	10.4 (s, 1H, NH), 6.9-7.4 (m, 5H, PhH), 3.5 (br s, 1H, NH)
26 [b]	456 (22000) 484 (19800)	1735, 1675, 1610, 1400	0.85, 1.60, 3.50 3.95	7.20	7.35-7.80 (m, 8H)

[a] Overlaps the substituent peaks. [b] Trifluoroacetic acid was used as the solvent for the nmr spectrum.

Reactions with binucleophiles were also carried out. *o*-Phenylenediamine afforded the red benzophenazine **33** on the basis of elemental analysis. Similarly, 2,3-diamino-1,4-naphthoquinone [21] gave the black dibenzophenazine **34** (62%) as shown by analysis and the ^1H nmr spectrum. Reaction of dithiooxamide with two moles of 2,3-dichloro-1,4-naphthoquinone produced the violet dithiazole derivative **35**, as previously [22] reported.

Table 8

^{13}C NMR Spectra of Mono-substituted-*N*-propylmaleimides

Compound No.	COCH=	COCNu	CH=	CNu=	CH_2	CH_2	CH_3	Substituent
17	167.4	172.3	84.3	149.0	38.8	21.7	11.0	131.6 117.6 46.3 (CH_2)
18	167.5	172.2	87.9	143.4	37.8	21.5	11.0	139.4 129.0 126.8 123.4
19	166.8	171.8	83.2	149.7	38.7	21.5	10.9	136.7 128.1 127.1 126.8 47.2 (CH_2)
20	167.4	172.4	85.2	153.9	38.7	21.5	10.9	144.2 130.6 121.1 115.6
21	165.9	169.3	108.6	144.7	39.6	21.8	11.1	132.0 130.9 109.5
22	165.0	168.3	116.6	153.8	39.8	21.6	11.0	144.3 130.6
23	171.1	177.0	106.1	142.2	39.0	21.4	11.0	159.7 (CO) 139.1 129.7 128.9 128.3 127.0 96.7
24	165.7	168.4	112.6	146.5	40.0	21.8	11.4	139.7 133.2 131.3 129.8 125.7 115.1
25	166.2	171.4	88.7	143.7	38.6	20.7	11.0	129.8 128.8 121.2 113.6

EXPERIMENTAL

The ^1H nmr spectra were taken on a EM-360 (60 MHz) and ^{13}C nmr on an FX-100 (25.0 MHz) spectrometer. The ir spectra were recorded with a Perkin-Elmer 283B instrument. Visible spectra were measured on a Perkin-Elmer 330 spectrophotometer. Melting points were determined on a Thomas-Hoover Capillary melting point apparatus without correction. Elemental analysis was conducted in this department under Dr. R. King. 3,3-Dichloro-*N*-phenylmaleimide **5** was prepared according to the literature method [13].

Preparation of 3,4-Bissubstituted-*N*-phenylmaleimides **6-11**.

3,4-Dichloro-*N*-phenylmaleimide (5 mmoles) was dissolved in absolute ethanol or anhydrous acetonitrile and the nucleophile (20 mmoles) was added. The reaction mixture was heated with stirring for 2 to 48 hours. The product precipitated out during the reaction. After cooling, the product was collected by filtration and recrystallized from methanol or ethanol (for details see Tables 1 and 2).

3-(2-Hydroxyanilino)-4-chloro-*N*-phenylmaleide (**12**).

Compound **12** had ^1H nmr (DMSO-d_6): 6.73-7.57 (m, 9H, Ar-H), 9.35 (s, 1H, NH) and 9.73 (s, 1H, OH); ^{13}C nmr: 166.3, 164.2 (C=O), 152.7, 139.9, 132.7, 131.6, 128.8, 127.8, 127.5, 126.6, 123.9, 118.5, 115.9 and 104.9; ir (bromoform): 3455 (OH), 3345 (NH), 1670 (C=O), 1660 (C=O), 1610 (C=C), 1600, 1500 cm^{-1}; ms: m/z 314 (M, 44.7%).

1,4-Benzothiazine-2,3-dicarboxylic Acid *N*-Phenylimide (**13**).

3,4-Dichloro-*N*-phenylmaleimide (1.21 g, 5 mmoles) and *o*-phenylenediamine (0.54 g, 5 mmoles) were refluxed in absolute ethanol (80 ml) with stirring for 15 hours. After cooling, the deep yellow product was filtered and recrystallized from ethanol; for details see Tables 1 and 2; ir (bromoform): 2250 (C=N), 1690 (C=O), 1640 (C=C), 1620 cm^{-1}; uv/vis(ethanol): 534 nm (9000), 478 nm (15000); insoluble in nmr solvents.

1-Phenyl-2-oxo-3-chloropyrrolo[4,5-*b*]quinoxaline (**14**).

The preparation was the same as above; for details see Tables 1 and 2; ir (bromoform): 1700 (C=O), 1650 (C=O), 1600, 1490 cm^{-1}; uv/vis (ethanol): 406 nm (10600).

2,2'-Bi-1,3-thiazole-4,4',5,5'-tetracarboxylic Acid Bis (*N*-phenylimide) (**15**).

The reaction mixture of 3,4-dichloro-*N*-phenylmaleimide, dithiooxamide and one equivalent of triethylamine was heated at 60° with stirring in dimethylformamide for 10 hours. After cooling, the dark brown solid was filtrated and washed with ethanol; for details see Tables 1 and 2; ir (bromoform): 1720, 1700, 1660, 1590 cm^{-1}; uv/vis (dimethylformamide): 500 (6000), 440 nm (11000).

3-Bromo-*N*-propylmaleimide.

The propylamine (0.5 mole) was added to the xylene solution of maleic anhydride (0.5 mole) at 80°. Xylene was stripped off until the reaction temperature reached 180° and the mixture was held at this temperature for 2 hours. *N*-Propylmaleimide was distilled under reduced pressure, yield 21%, mp 32-33° (lit [18] mp 30.5-31.5°).

The *N*-propylmaleimide (27.8 g, 0.2 mole) was dissolved in 20 ml of carbon tetrachloride, and 32.0 g (0.2 mole) of bromine was added slowly at 0° with stirring. After standing for two hours the unreacted bromine was allowed to evaporate spontaneously to give an oily product; ^1H nmr (deuteried chloroform): 4.80 (s, 2H, CHBr), 3.55 (t, 2H, NCH_2), 2.65 (m, 2H), 1.85 (t, 3H, CH_3).

N-Propyldibromosuccinimide (14.85 g, 0.05 mole) and 4.59 g (0.056 mole) of anhydrous sodium acetate were refluxed vigorously for 5 hours in 95% ethanol (40 ml). Direct sunlight was avoided during the reaction. The precipitate of sodium bromide was removed by filtration, and the ethanol was distilled off. The crude product crystallized from ethyl ether as white crystals (9.75 g, 90%), mp 36-38°; ^1H nmr (deuteriochloroform): 6.90 (s, 1H, CH=), 3.60 (t, 2H, NCH_2), 1.70 (m, 2H, CH_2), 0.91 (t, 3H, CH_3); ^{13}C nmr: 168.2 (C=O), 164.8 (C=O), 131.4, 130.5, 39.0, 21.3, 10.7.

Anal. Calcd. for $C_7H_8BrNO_2$: C, 38.74; H, 3.69; N, 6.45. Found: C, 39.10; H, 3.77; N, 6.24.

Preparation of 3-Monosubstituted-*N*-propylmaleimides **17-26**.

3-Bromo-*N*-propylmaleimide (1.74 g, 8 mmoles) and the appropriate nitrogen containing nucleophile (16 mmoles) were refluxed with stirring in absolute ethanol (20 ml) for 4 hours to 2 days. The reaction mixture was cooled and the product was collected by filtration and recrystallized from methanol (for details see Table 5).

2,3-Di(1-pyrazolyl)-1,4-naphthoquinone (**28**).

Compound **28** had mp 200-201°, (lit [15] mp 201°); ^{1}H nmr (DMSO-d_6): 8.05 (m, 4H), 7.78 (d, 2H, Py-H), 7.52 (d, 2H, Py-H), 6.39 (d-d, 2H, Py-H); ^{13}C nmr: 179.8 (C=O), 141.4, 140.2, 134.8, 133.9, 130.6, 126.5.

2-Hydroxy-3-(1-pyrazolyl)-1,4-naphthoquinone (**29**).

2,3-Di(1-pyrazolyl)-1,4-naphthoquinone (1.00 g) was dissolved in 60 ml of tetrahydrofuran and a sodium hydroxide solution (0.35 g in 10 ml water) was added. The solution turned dark red and after 0.5 hours the solution was evaporated. The dark red residue was dissolved in 30 ml of water and acidified with dilute hydrochloric acid. An orange precipitate was formed. After filtration it was recrystallized, mp 217-218.5°; ^{1}H nmr (DMSO-d_6): 8.06 (m, 2H), 8.01 (d-d, 1H), 7.88 (m, 2H), 7.79 (d-d, 1H), 6.52 (d-d, 1H), 3.60 (br, 1H, OH); ^{13}C nmr: 181.4 (C=O), 179.0 (C=O), 139.3, 134.9, 133.5, 133.2, 131.3, 130.0, 126.2, 126.0, 121.6, 106.0; ir (bromoform): 3450 (OH), 1690 (C=O), 1590, 1250 cm^{-1}; uv/vis (methanol): 422 nm (2018) and 444 nm (2510); m/z 240 (M$^+$, 64%), 212, 184, 156, 105.

Anal. Calcd. for $C_{13}H_8N_2O_3$: C, 65.00; H, 3.36; N, 11.66. Found: C, 64.69; H, 3.26; N, 11.38.

1-(1,4-Dihydro-1,4-dioxo-3-hydroxy-2-naphthyl)-4-(dimethylamino)pyridinium Betaine (**31**).

2,3-Dichloro-1,4-naphthoquinone (1.00 g), and 1.29 g dimethylaminopyridine was refluxed in 20 ml of dry dimethylformamide. Insoluble orange material was filtered off and recrystallized from dimethyl sulfoxide and gave a reddish product, mp >350°; ^{1}H nmr (DMSO-d_6): 8.01 (d, 2H, PyH), 7.87-7.60 (m, 4H), 6.98 (d, 2H, PyH), 3.22 (s, 6H, NMe_2); ir (potassium bromide): 1690, 1650, 1590, 1225 cm^{-1}; uv/vis (ethanol): 465 nm (9000).

2-Hydroxy-3-[1-(4-pyridonyl)]-1,4-naphthoquinone (**32**).

2,3-Dichloro-1,4-naphthoquinone (1.00 g) was mixed with 1.68 g of 4-pyridone and refluxed for 24 hours in acetonitrile. An orange precipitate was obtained. The product was extremely difficult to dissolve. Recrystallization in 95% acetic acid gave **32**, yield 63%, mp >300°; ^{1}H nmr (DMSO-d_6): 8.27 (d, 2H, Py-H), 7.79-7.62 (m, 4H), 7.13 (d, 2H, Py-H) and 3.92 (br, 1H, OH); ir (potassium bromide): 3450 (OH), 1680 (C=O), 1640 (C=O), 1580 cm^{-1}; m/z 267 (M$^+$, 100%); uv/vis (ethanol): 430 nm (11000).

Anal. Calcd. for $C_{15}H_9NO_4$: C, 67.40; H, 3.39; N, 5.24. Found: C, 67.23; H, 3.41; N, 5.10.

6-Chloro-5-hydroxybenzo[*b*]phenazine (**33**).

The reaction mixture of 2,3-dichloro-1,4-naphthoquinone and *o*-phenylenediamine was refluxed in ethanol for 10 hours. After cooling, the deep red solid was filtered off and washed with ethanol, yield 65%, mp 263-265° (lit [18] mp 268°); ^{1}H nmr (DMSO-d_6): 7.5-8.3 (m); ir (bromoform): 2250, 1580, 1520 cm^{-1}; uv/vis (ethanol): 512 (11430), 434 nm (7360).

Anal. Calcd. for $C_{16}H_9ClN_2O$: C, 68.44; H, 3.21; N, 9.98. Found: C, 68.82; H, 3.20; N, 9.83.

6,13-Dihydro-5,7,12,14-tetraoxabisnaphtho[2,3-*b*:2,3-*e*]pyrazine (**34**).

This compound was prepared as above, yield 62%, mp >300°; ^{1}H nmr (DMSO-d_6): 7.7-8.4 (m); ir (bromoform): 2250, 1660, 1610, 1580, 1490 cm^{-1}; uv/vis (dimethylformamide): 600 nm; uv/vis (potassium bromide): 640 nm (900).

Anal. Calcd. for $C_{20}H_{10}N_2O_4$: C, 70.07; H, 2.97; N, 8.28. Found: C, 69.75; H, 3.18; N, 8.49.

Bisnaphtho[2,3-*d*:2,3-*d'*]-2,2'-bi-1,3-thiazole (**35**).

The reaction mixture of 2,3-dichloro-1,4-naphthoquinone, dithiooxamide and triethyl amine was heated in dimethylformamide with stirring at 50° for 10 hours, a solid was formed and collected by filtration and washed with ethanol, yield 57%, mp > 300°; ir (bromoform): 1650, 1580 and 1530 cm^{-1}; uv/vis (dimethylformamide): 500, 480 nm.

Anal. Calcd. for $C_{22}H_8N_2O_4S_2$: C, 61.68; H, 1.88; N, 6.54. Found: C, 62.05; H, 2.11; N, 6.80.

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