Octa-alkoxy Phthalocyanine and Naphthalocyanine Derivatives: Dyes with Q-Band Absorption in the Far Red or Near Infrared

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The lithium alkoxide-catalysed cyclic tetramerisation of various 3,6-dialkoxy-4,5-dichlorophthalo-nitriles, 1,4-dialkoxynaphthalene-2,3-dicarbonitriles and 3,6-dialkoxyphthalonitriles to give the corresponding metal-free octa-alkoxyoctachlorophthalocyanines, octa-alkoxynaphthalocyanines and octa-alkoxyphthalocyanines is described. An unexpected *trans*-alkoxylation reaction occurs during the cyclisation of the first two series of precursors. Metal-free phthalocyanines and naphthalo-cyanines have been converted into derivatives containing various metal ions. Compounds show Q-band absorption in the region 739—862 nm in toluene solution. The fluorescence spectra of selected examples are reported. The solubility of some of the compounds has been measured in a formulation of liquid crystal materials.

Compounds which absorb strongly at wavelengths of laser light can, in principle, be exploited as guest dyes dissolved in liquid crystalline host materials in a laser addressed system. Such devices utilize absorption of laser energy by the dye to cause local heating which alters optical properties in otherwise transparent liquid crystals. Particular applications are in laser addressed storage systems and projection displays in which light is directed through a cell containing the material and projected onto a screen. $Ga_xAl_{1-x}As$ lasers (where $x = 0$—1) provide laser light in the range of *ca.* 850 nm for gallium arsenide down to *ca.* 750 nm as the aluminium content is increased. Thus light-absorbing compounds are required which match these lasers; the materials should also be at least partially soluble in the liquid crystal medium.

Phthalocyanines show strong absorption in the visible region (Q-band), *e.g.* metal-free phthalocyanine, H_2Pc, $\lambda_{max.}$ 665 and 698; copper phthalocyanine, CuPc, $\lambda_{max.}$ 678 nm.[1] The band is shifted further to the red when substituents are introduced onto the benzene rings, particularly at sites α to the point of fusion to the heterocyclic ring (the '3,6' positions).[2] Linear benzoannulation also gives rise to bathochromic shifts as exemplified by 2,3-naphthalocyanine (NPc), $\lambda_{max.}$ 780 nm.[3] There is, therefore, potential for tuning the Q-band absorption to match the wavelengths of GaAlAs laser light. However, the problem of the low solubility of the Pc ring system in organic solvents also needs to be overcome if the application of these materials in the devices outlined above is to be realised.

As part of a research programme into Pc derivatives we have addressed the problem of insolubility by introducing bulky or long chain substituents at the α positions. Substituents so placed should cause substantial disruption of the strong lattice forces of the parent Pc and hence help confer solubility. Considerable success has been achieved with straight-chain alkyl groups.[4] The present paper describes the synthesis and spectroscopic properties of Pc and NPc derivatives bearing alkoxy groups with chain lengths varying between C_1 and C_{12}. These groups give rise to substantial bathochromic shifts of the Q-band. We also report the solubility of representative materials in liquid crystals.

Results and Discussion

Preparative Work.—The compounds originally sought in this study fall into three series, classified according to the

substituents or modification of the Pc structure. We refer to the first series, investigated as the metal-free derivatives and in one case as the copper complex, as octachloro-octa-alkoxy-phthalocyanines $(Cl\cdot RO)_8H_2Pc$ **(1)** and $(Cl\cdot RO)_8CuPc$ **(2)**. The second and third series, obtained as the metal-free and in some instances as copper, zinc, or nickel complexes, we designate respectively as octa-alkoxynaphthalocyanines $[(RO)_8H_2NPc$ **(3)** and $(RO)_8CuNPc$ **(4)**], and octa-alkoxy-phthalocyanines $[(RO)_8H_2Pc$ **(5)**, $(RO)_8CuPc$ **(6)**, $(RO)_8ZnPc$ **(7)**, and $(RO)_8NiPc$ **(8)**].

A convenient method for preparing Pc derivatives is to treat a phthalonitrile with a lithium alkoxide. This induces the required cyclic tetramerisation reaction to give the Pc as the lithiated derivative which on acidic work-up is converted into the metal-free analogue. Thus, in principle, for the present study the immediate precursors to the Pc and NPc derivatives are the appropriately substituted dialkoxy dinitriles **(9)**, **(10)**, and **(11)**. These were prepared by standard alkylations of the dicyano-hydroquinones **(12)**, **(13)**, and **(14)**. Most were recrystallised for combustion analysis (see Table 1). However, in two cases (see Experimental section) the product isolated from the reaction mixture was used directly in the tetramerisation reaction without further purification. In these cases, confirmation of structure was based on n.m.r. and i.r. spectroscopic data.

Previously, Witkiewicz *et al.*[5] converted **(11a)** into **(5a)** using lithium pentanolate in pentanol: they subsequently obtained from **(5a)** the copper and zinc complexes. In the present work, 4,5-dichloro-3,6-dimethoxyphthalonitrile **(9a)** was treated with lithium pentanolate in pentanol and the reaction worked up in acetic acid. The resulting product showed an unexpectedly low m.p., 71—73 °C, and was readily soluble in toluene and methylene dichloride. The material showed u.v.–visible absorption bands consistent with formation of the Pc ring system (*i.e.* Soret and Q-band). However, the ^1H n.m.r. spectrum revealed that the product was not the expected octamethoxy compound **(1a)**, there being signals for protons in pentyloxy side-chains as well as a singlet for a methoxy side-chain. Microanalytical data on the material showed that the chlorine atoms had been retained. Thus at some stage during the reaction an unexpected *trans*-alkoxylation had occurred giving rise to incorporation of pentyloxy groups at the expense of the methoxy substituents. Integration of appropriate signals in the n.m.r. spectrum revealed that *ca.* 75% of the methoxy groups had been exchanged by pentyloxy groups. Using the
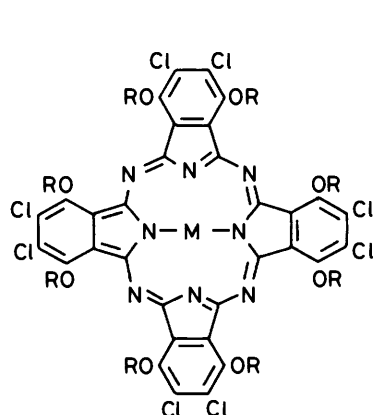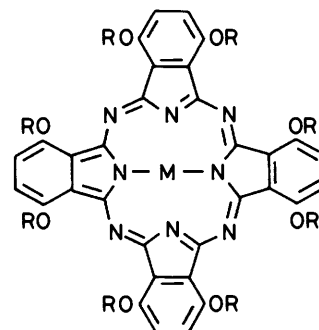
(1) M = H, H;
a R = Me
b R = Et
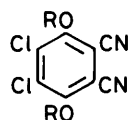c R = Pr
d R = Bu
e R = Pentyl

(2) M = Cu, R = Pentyl
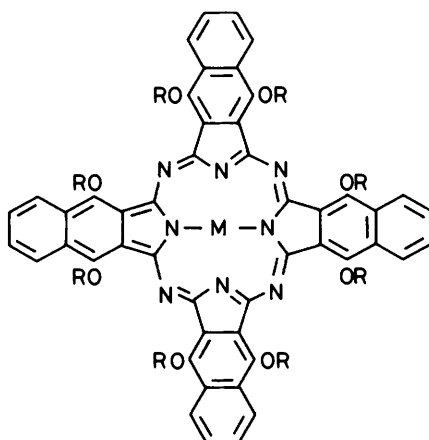
(3) M = H, H;
a R = Et
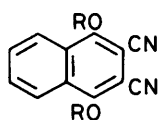b R = Pr
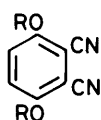c R = Bu
d R = Pentyl
e R = Octyl

(4) M = Cu, R = Pentyl

(5) M = H, H;
a R = Me
b R = Et
c R = Pr
d R = Bu
e R = Pentyl
f R = Hexyl
g R = Heptyl
h R = Octyl
i R = Nonyl
j R = Decyl
k R = Dodecyl
l R = Pent-4-enyl
m R = 3-Phenylpropyl

(6) M = Cu;
a R = Pr
b R = Bu
c R = Pentyl
d R = Octyl
e R = Dodecyl
f R = Pent-4-enyl

(7) M = Zn, R = Pentyl

(8) M = Ni, R = Pentyl

(9)
a R = Me
b R = Et
c R = Pr
d R = Bu
e R = Pentyl

(12) R = H

(10)
a R = Me
b R = Et
c R = Pr
d R = Bu
e R = Octyl

(13) R = H

(11)
a R = Me
b R = Et
c R = Pr
d R = Bu
e R = Pentyl
f R = Hexyl
g R = Heptyl
h R = Octyl
i R = Nonyl
j R = Decyl
k R = Dodecyl
l R = Pent-4-enyl
m R = 3-Phenyl-propyl

(14) R = H

same reaction conditions, 1,4-dimethoxynaphthalene-2,3-dicarbonitrile (10a) afforded a soluble red–brown material having both a Soret band and a Q-band in the u.v.–visible spectrum. The ^{1}H n.m.r. spectrum showed that trans-alkoxylation had again occurred with the ratio of pentyloxy groups to methoxy groups being 9:1. In a subsequent reaction exchange was complete as judged from the ^{1}H n.m.r. spectrum and satisfactory analytical data.

The cyclic tetramerisation of (9a) and (10a) was investigated in other alcohols using the corresponding lithium and, in one case, sodium alkoxide as base. Results showing the extent of the alkoxide exchanges in the derived (Cl·RO)$_8$H$_2$Pc's and (RO)$_8$H$_2$NPc's are given in Table 2. In subsequent experiments 4,5-dichloro-3,6-dipropoxyphthalonitrile (9c) was cyclised in pentan-1-ol–lithium pentanolate to give a mixed pentyloxy/

propoxy (Cl·RO)$_8$H$_2$Pc (ratio of groups 87:13). There was no evidence of alkoxide exchange when (Cl·MeO)$_8$H$_2$Pc or (MeO)$_8$H$_2$NPc were treated with lithium or sodium pentanolate in pentan-1-ol. From this we deduce that the observed displacements probably occur via reactions on either the starting dinitrile or an intermediate.

Samples of (Cl·RO)$_8$H$_2$Pc and (RO)$_8$H$_2$NPC containing but one type of alkoxy group were prepared in a subsequent series of reactions in which the dialkoxy dinitrile precursors (9) and (10) were treated with the corresponding alkoxide/alcohol (see Table 3). Where direct comparisons are possible it is apparent that yields of recovered product are higher for the (Cl·RO)$_8$-H$_2$Pc series. A problem arose when cyclising the longer chain 1,4-dialkoxynaphthalene-2,3-dicarbonitrile (10e) because of the low reactivity of lithium in the long-chain alcohol. This was overcome by generating the lithium alkoxide by treating the alcohol with a solution of 1.5M butyl-lithium.

3,6-Dialkoxyphthalonitriles (11) were converted into the corresponding (RO)$_8$H$_2$Pc's (5) using either lithium pentanolate in pentan-1-ol or lithium butoxide in butan-1-ol (Table 3). There was no evidence of trans-alkoxylation in this series of reactions. Thus the trans-alkoxylation reaction is apparently promoted by the presence of the electron-withdrawing chlorine substituents and benzo fusion, features consistent with an S_NAr mechanism.

The copper, zinc, and nickel complexes reported in Table 4 were prepared from the metal-free derivatives and the appropriate metal acetate using quinoline, butan-1-ol, or pentan-1-ol as solvents and heating the solution to reflux. Although reaction temperatures were lower using the alcohols as solvent, yields were higher, largely because of the greater ease of recovering the product.

Electronic Spectra.—The Pc system is characterised[7,8] by strong absorption bands in the u.v. region (the Soret band) and in the visible region (the Q-band); low intensity bands in the

Table 1. Preparation of some 3,6-dialkoxy-4,5-dichlorophthalonitriles (9), 1,4-dialkoxynaphthalene-2,3-dicarbonitriles (10), and 3,6-dialkoxy-phthalonitriles (11) from the dicyanohydroquinones (12), (13), and (14)

Compound no.	SM[a]	Alkylating agent[b]	Time (h)	Yield (%)	M.p. (°C)	Molecular formula	Found (%)			Requires (%)		
							C	H	N	C	H	N
(9a)	(12)	CH$_2$N$_2$	0.75	67	186[c]							
(9b)	(12)	EtI	60	55	97	C$_{12}$H$_{10}$Cl$_2$N$_2$O$_2$	50.7	3.4	9.75	50.5	3.5	9.8
(9c)	(12)	PrI	60	48	60	C$_{14}$H$_{14}$Cl$_2$N$_2$O$_2$	53.7	4.7	8.75	53.7	4.5	8.95
(9d)	(12)	BuI	56	52	51	C$_{16}$H$_{18}$Cl$_2$N$_2$O$_2$	56.5	5.3	8.25	56.3	5.3	8.2
(10a)	(13)	CH$_2$N$_2$	0.5	80	187[d]							
(10b)	(13)	EtI	72	40	169—171	C$_{16}$H$_{14}$N$_2$O$_2$	71.9	5.3	10.4	72.2	5.3	10.5
(10c)	(13)	PrI	60	43	91—93	C$_{18}$H$_{18}$N$_2$O$_2$	73.35	6.1	9.5	73.4	6.2	9.5
(10d)	(13)	BuI	60	58	67—69	C$_{20}$H$_{22}$N$_2$O$_2$	74.2	6.95	8.5	74.5	6.9	8.7
(10e)	(13)	Octyl I	60	42	38	C$_{28}$H$_{38}$N$_2$O$_2$	77.3	8.8	6.3	77.4	8.8	6.45
(11b)	(14)	EtI	60	48	203	C$_{12}$H$_{12}$N$_2$O$_2$	66.5	5.6	12.9	66.65	5.6	12.95
(11c)	(14)	PrI	48	40	198	C$_{14}$H$_{16}$N$_2$O$_2$	68.7	6.7	11.5	68.8	6.6	11.5
(11d)	(14)	BuI	60	50	193	C$_{16}$H$_{20}$N$_2$O$_2$	70.4	7.5	10.2	70.55	7.4	10.3
(11e)	(14)	Pentyl I	60	58	172	C$_{18}$H$_{24}$N$_2$O$_2$	72.2	7.95	9.3	72.0	8.05	9.3
(11f)	(14)	Hexyl I	60	48	164	C$_{20}$H$_{28}$N$_2$O$_2$	73.3	8.45	8.5	73.1	8.6	8.5
(11g)	(14)	Heptyl I	60	52	153	C$_{22}$H$_{32}$N$_2$O$_2$	73.9	9.0	7.7	74.1	9.05	7.85
(11i)	(14)	Nonyl I	60	47	151	C$_{26}$H$_{40}$N$_2$O$_2$	75.3	9.7	7.1	75.7	9.8	6.8
(11j)	(14)	Decyl I	60	49	142	C$_{28}$H$_{44}$N$_2$O$_2$	76.0	10.1	6.3	76.3	10.05	6.4
(11k)	(14)	Dodecyl I	65	47	137	C$_{32}$H$_{52}$N$_2$O$_2$	77.5	10.75	5.7	77.4	10.5	5.65
(11l)	(14)	CH$_2$=CH(CH$_2$)$_3$I	65	42	178	C$_{18}$H$_{20}$N$_2$O$_2$	72.8	6.9	9.45	72.95	6.8	9.45
(11m)	(14)	Ph(CH$_2$)$_3$I	60	35	170	C$_{26}$H$_{24}$N$_2$O$_2$	78.65	5.9	7.0	78.75	6.1	7.1

[a] Starting material. [b] Straight-chain alkyl groups are used throughout. [c] Lit.,[6] 187 °C. [d] Lit.,[6] 189 °C.

Table 2. Reactions of 4,5-dichloro-3,6-dimethoxyphthalonitrile (9a) and 1,4-dimethoxynaphthalene-2,3-dicarbonitrile (10a) with ROH/RO⁻ to give (Cl·MeO/RO)$_8$H$_2$Pc and (MeO/RO)$_8$H$_2$NPc

Entry	SM	Solvent	Base	Time (h)	Temp. (°C)	Ratio of MeO:RO groups in product
A	(9a)	EtOH	EtOLi	0.75	150	1:6.5[a]
B	(9a)	PentylOH	PentylOLi	1	Reflux	1:7[b]
C	(9a)	PentylOH	PentylONa	0.5	Refux	1:3[b]
D	(10a)	EtOH	EtOLi	0.75	150	1:8.8[b]
E	(10a)	PrOH	PrOLi	0.75	150	1:9.7[b]
F	(10a)	BuOH	BuOLi	0.5	Reflux	1:34[b]
G	(10a)	PentylOH	PentylOLi	0.5	Reflux	1:9,[b] 0:1[c]

[a] Estimated by C, H, N elemental analysis data. [b] Estimated from ¹H n.m.r. spectral data. [c] No MeO signal in ¹H n.m.r. spectrum. Material gives satisfactory C, H, N analysis for (PentylO)$_8$H$_2$NPc, see Table 3.

visible region to shorter wavelength of the Q-band are vibronic in origin. Metal Pcs and metal-free Pcs have D_{4h} and D_{2h} symmetry respectively and the degeneracy of the lowest-energy singlet state in the former is lifted in the latter by a rhombic distortion. Thus unlike the spectra of metal Pcs, those of metal-free derivatives may show a characteristic splitting of the Q-band into the Q$_x$ and Q$_y$ components provided that the rhombic distortion is larger than the optical bandwidth.

Q-Band absorption data obtained for representative compounds in toluene solution are collected in Table 5. In addition to wavelengths, the energies and energy separation, Δ, of the Q$_x$ and Q$_y$ bands are given in the cases where splitting is observed.

The variations in $\lambda_{max.}$ in Table 5 reveal how benzoannulation, substituents, and central ion provide a means of tuning the wavelength of the Q-band absorption in the far red–near i.r. region of the spectrum. The largest bathochromic shift is observed for the (RO)$_8$NPcs. Comparison of the $\lambda_{max.}$ 862 nm in these compounds with that in unsubstituted naphthalocyanine $\lambda_{max.}$ 780 nm[3] illustrates the sensitivity of the Q-band to alkoxy

substituents located α to the point of fusion with the heterocyclic rings. A broadly comparable shift is apparent in the Pc series where (RO)$_8$H$_2$Pcs absorb at ca. 740 and 760 nm, well to the red of the Q-band in H$_2$Pc 665 and 698 nm.[1] In contrast, a Pc derivative fused via eight ether linkages at the '4,5-positions' (to four crown ether moieties) shows Q-band absorption at 690 nm.[9] That the Q-band absorption is more red shifted by substituents at the 3,6-positions than by those at the 4,5-positions is apparent from earlier studies. Thus octa-3,6-chloro CuPc shows $\lambda_{max.}$ 705 nm, 10 nm to the red of the Q-band in octa-4,5-chloro CuPc.[2b] Similarly, the Q$_x$ and Q$_y$ bands in octa-3,6-butyl H$_2$Pc, 695 and 727 nm,[4] are to the red of those in octa-4,5-butyl H$_2$Pc, 673 and 708 nm.[10] However, the magnitude of the effect is clearly much larger when the substituent involves an ether linkage. Substantial red shifts have also been reported for Pcs bearing sulphide linkages at the 3,6-positions.[11] The Q-bands for the (Cl·RO)$_8$H$_2$Pcs are marginally to the blue of those for the corresponding (RO)$_8$H$_2$Pcs. Data obtained for the former series also show a chain-length dependence. Thus (Cl·MeO)$_8$H$_2$Pc, in particular, absorbs at shorter wavelengths than the derivatives bearing longer chains.

Splitting for the Q-band absorption in the spectra of the metal-free compounds differs from one series to another. Among the (Cl·RO)$_8$H$_2$Pcs the Q$_x$ and Q$_y$ bands are best resolved when RO is methoxy or ethoxy. The values for Δ are comparable (480 and 490 cm⁻¹). However, when RO is pentyloxy the Q$_x$ absorption appears only as a shoulder. All of the (RO)$_8$H$_2$Pc compounds examined as solutions in toluene show two well resolved lines. Values for Δ within this series again show no significant variation (390—430 cm⁻¹) but are lower than those for the (Cl·RO)$_8$H$_2$Pcs. Spectra obtained of (RO)$_8$H$_2$Pcs in dichloromethane show loss of resolution of the two bands which is probably due to aggregation in this solvent. Spectra recorded of 10⁻⁴ and 10⁻⁵M solutions in dichloromethane are identical in shape implying that if aggregation is indeed the cause then it is present even at 10⁻⁵M concentration. Members of the (RO)$_8$H$_2$NPc series show only a single band even in toluene as does H$_2$NPc itself in the solvent chloronaphthalene.[3] The magnitude of Δ is a measure of the departure of the system from

Table 3. Preparation of some $(Cl\cdot RO)_8H_2Pc$'s (1), $(RO)_8H_2NPc$'s (3), and $(RO)_8H_2Pc$'s (5)

	Compound		ROH/ ROLi (ROH)b	Time (h)	Temp. (°C)	Yield (%)	M.p. (°C)	Molecular formula	Found			Requires (%)		
No.	RO^b	SM^a							C	H	N	C	H	N
(1a)	MeO	(9a)	MeOH	0.5	150	55	>300	$C_{40}H_{26}Cl_8N_8O_8$	46.2	2.6	10.8	46.6	2.5	10.9
(1b)	EtO	(9b)	EtOH	0.5	85	28	>300	$C_{48}H_{42}Cl_8N_8O_8$	50.7	3.6	9.7	50.45	3.7	9.8
(1c)	PrO	(9c)	PrOH	0.75	Reflux	33	>300	$C_{56}H_{58}Cl_8N_8O_8$	53.9	4.6	8.8	53.6	4.65	8.9
(1d)	BuO	(9e)	BuOH	0.75	Reflux	31	>300	$C_{64}H_{74}Cl_8N_8O_8$	55.9	5.4	8.1	56.2	5.5	8.2
(1e)	PentylO	(9f)	PentylOH	0.75	Reflux	33	>300	$C_{72}H_{90}Cl_8N_8O_8$	58.8	6.0	7.7	58.5	6.1	7.6
(3a)	EtO	(10b)	EtOH	0.75	85	10	>300	$C_{64}H_{58}N_8O_8$	71.6	5.5	10.4	72.3	5.1	10.5
(3b)	PrO	(10c)	PrOH	0.75	Reflux	15	>300	$C_{72}H_{74}N_8O_8$	72.65	6.3	9.3	73.3	6.3	9.5
(3c)	BuO	(10d)	BuOH	0.75	Reflux	17	303	$C_{80}H_{90}N_8O_8$	74.15	7.15	8.65	74.4	7.0	8.7
(3d)	PentylO	(10a)	PentylOH	0.5	Reflux	30	287—289	$C_{88}H_{106}N_8O_8$	75.0	7.7	7.8	75.3	7.6	8.0
(3e)	OctO	(10e)	OctylOH	1	145—150	15	148	$C_{112}H_{154}N_8O_8$	77.2	9.3	6.3	77.3	8.9	6.45
(5b)	EtO	(11b)	PentylOH	0.75	Reflux	20	>250	$C_{48}H_{50}N_8O_8$	67.0	6.1	12.5	66.6	5.8	12.9
(5c)	PrO	(11c)	PentylOH	0.75	Reflux	23	>250	$C_{56}H_{66}N_8O_8$	68.8	6.6	11.4	68.7	6.8	11.4
(5d)	BuO	(11d)	BuOH	1	Reflux	21	136.5—138.5	$C_{64}H_{82}N_8O_8$	70.4	7.7	10.0	70.4	7.6	10.2
(5e)	PentylO	(11e)	PentylOH	0.75	Reflux	28	116—117.5	$C_{72}H_{98}N_8O_8$	71.8	8.1	9.3	71.8	8.2	9.3
(5f)	HexO	(11f)	PentylOH	0.75	Reflux	32	85—86.5	$C_{80}H_{114}N_8O_8$	72.65	8.7	8.7	73.0	8.7	8.5
(5g)	HepO	(11g)	PentylOH	0.75	Reflux	33	76.5—77.5	$C_{88}H_{130}N_8O_8$	73.9	9.2	8.0	74.0	9.2	7.85
(5h)	OctO	(11h)	PentylOH	0.75	Reflux	37	66—67	$C_{96}H_{146}N_8O_8$	74.5	9.7	7.4	74.85	9.55	7.3
(5i)	NonO	(11i)	PentylOH	0.75	Reflux	37	49—50.5	$C_{104}H_{162}N_8O_8$	75.2	9.75	7.0	75.6	9.9	6.8
(5j)	DecO	(11j)	PentylOH	0.75	Reflux	38	51—53	$C_{112}H_{178}N_8O_8$	75.95	10.4	6.45	76.2	10.1	6.35
(5k)	DodecO	(11k)	PentylOH	0.75	Reflux	40	53—54	$C_{128}H_{210}N_8O_8$	77.0	10.8	5.85	77.3	10.6	5.6
(5l)	Pent-4-enylO	(11l)	PentylOH	0.75	Reflux	35	117.5—119.5	$C_{72}H_{82}N_8O_8$	72.5	7.2	9.5	72.8	7.0	9.4
(5m)	Ph(CH$_2$)$_3$O	(11m)	PentylOH	0.75	Reflux	23	>300	$C_{104}H_{98}N_8O_8$	78.3	6.0	6.7	78.65	6.2	7.05

^a SM = starting material. ^b R = straight chain. ^c As reported in Table 2.

Table 4. Preparations of metal derivatives of some alkoxy substituted phthalocyanines by treating the metal-free derivative with the appropriate metal acetate

	Compound			Time (h)	Temp. (°C)	Yield (%)	M.p. (°C)	Molecular formula	Found (%)			Requires (%)		
No.	RO	Metal	Solvent						C	H	N	C	H	N
(2)	PentylO	Cu	PentylOH	0.5	Reflux	78	>300	$C_{72}H_{88}Cl_8CuN_8O_8$	56.4	5.6	7.5	56.1	5.75	7.3
(4)	PentylO	Cu	Quinoline	1.0	Reflux	23	292—294 (decomp.)	$C_{88}H_{104}CuN_8O_8$	71.9	7.4	7.2	72.1	7.15	7.6
(6a)	PrO	Cu	BuOH	0.5	Reflux	81	>300	$C_{56}H_{64}CuN_8O_8$	64.6	6.2	10.7	64.6	6.2	10.8
(6b)	BuO	Cu	BuOH	0.5	Reflux	77	200—201	$C_{64}H_{80}CuN_8O_8$	67.1	7.3	9.4	66.7	7.0	9.7
(6c)	PentylO	Cu	PentylOH	0.5	Reflux	85	173.5—174.5	$C_{72}H_{96}CuN_8O_8$	68.4	7.6	8.8	68.35	7.65	8.9
(6d)	OctylO	Cu	PentylOH	0.5	Reflux	81	69	$C_{96}H_{144}CuN_8O_8$	71.7	9.1	7.1	72.0	9.1	7.0
(6e)	DodecylO	Cu	PentylOH	0.5	Reflux	79	52—53.5	$C_{128}H_{208}CuN_8O_8$	74.85	10.4	5.4	75.0	10.2	5.5
(6f)	Pent-4-enylO	Cu	PentylOH	0.5	Reflux	78	171.5—173	$C_{72}H_{80}CuN_8O_8$	69.0	6.8	8.9	69.2	6.45	9.0
(7)	PentylO	Zn	PentylOH	0.5	Reflux	71	139—141	$C_{72}H_{96}N_8O_8Zn$	68.5	7.4	9.0	68.25	7.6	8.8
(8)	PentylO	Ni	PentylOH	0.5	Reflux	68	198—200	$C_{72}H_{96}N_8NiO_8$	68.65	7.6	8.7	68.6	7.7	8.9

D_{4h} symmetry.[8] The splittings in metal-free tetra-azaporphin is 2 100 cm^{-1}. Fusion of four benzene rings to this system to give the Pc nucleus shifts the Q-band to the red as the conjugation is extended out to the benzene rings. It follows that the perturbation of the D_{4h} symmetry by the two central hydrogens becomes less significant and the Q-band splitting is correspondingly lowered to 730 cm^{-1}. Thus, there is a correlation between the energy of the centroid of the Q-bands and the energy splitting of the bands, the lower the energy the smaller the value of Δ. The incorporation of substituents to give the present series continues the trend, the Q-band splitting decreasing on going from $(Cl\cdot EtO)_8H_2Pc$ to $(EtO)_8H_2Pc$ as the Q-band is shifted further to the red. The apparent absence of Q-band splitting in the spectra of the $(RO)_8H_2NPcs$ may, therefore, arise through further continuation of this effect.

Fluorescence spectra were recorded for an example of a metal-free derivative from each of the three series. $(Cl\cdot MeO)_8H_2Pc$ (1a) and $(C_5H_{11}O)_8H_2NPc$ (3d) were measured at room temperature as solutions in chloroform and values for the corrected $\lambda_{max.}$ emission are 745 and ca. 890 nm respectively.

For $(C_5H_{11}O)_8H_2Pc$ (5e) in toluene at room temperature, the emission is at $\lambda_{max.}$ 771 nm (uncorrected).

Solubility in a Nematic Liquid Crystal.—The long wavelength Q-band absorption and the window in the visible region which are characteristic of the present compounds can, in principle, be exploited in laser addressed systems. With the exception of the octa-methoxy derivative (1a), which is only sparingly soluble in chloroform and toluene, the compounds prepared in this study show satisfactory solubility in aromatic hydrocarbon solvents, chloroform, and dichloromethane. Quantitative room-temperature solubility data (w/w) were obtained for $(C_5H_{11}O)_8H_2Pc$ (5e) in CHCl$_3$ (21%), xylene (10%), and 2-ethoxyethyl acetate (0.5%) and for $(C_{12}H_{25}O)_8H_2Pc$ (5k) in xylene (10%). The solubility in simple solvents prompted us to investigate the solubility of samples in the nematic liquid crystal E7. The latter is a commercially available (B.D.H. Chemicals, Poole, Dorset) formulation of cyanobiphenyls and cyanoterphenyls. Twelve samples were investigated including two mixed methoxy/alkoxy materials, namely the products from the entries A and F in

Table 5. Q-Band absorption data for some $(Cl \cdot RO)_8 Pcs$, $(RO)_8 NPcs$, and $(RO)_8 Pcs$

No.	Abbreviation	Solvent	$\lambda_{max.}/nm$ ($\varepsilon \times 10^{-5}$)		$\nu_{max.}/cm^{-1}$		Δ/cm^{-1} [a]
			Q_x	Q_y	Q_x	Q_y	
(1a)	$(Cl \cdot MeO)_8 H_2 Pc$	Toluene	711	736 (b)	14 070	13 590	480
(1b)	$(Cl \cdot EtO)_8 H_2 Pc$	Toluene	726 (1.20)	753 (1.35)	13 770	13 280	490
(1e)	$(Cl \cdot PentylO)_8 H_2 Pc$	Toluene	~735 (s)	756 (1.36)			
(2)	$(Cl \cdot PentylO)_8 CuPc$	Toluene		739 (1.35)			
(3c)	$(BuO)_8 H_2 NPc$	Toluene		862 (1.81)			
(3e)	$(OctylO)_8 H_2 NPc$	Toluene		862 (1.82)			
(4)	$(PentylO)_8 CuNPc$	Toluene		849 (2.34)			
(5b)	$(EtO)_8 H_2 Pc$	Toluene	734 (1.16)	758 (1.38)	13 620	13 190	430
(5c)	$(PrO)_8 H_2 Pc$	Toluene	737 (1.17)	760 (1.35)	13 570	13 160	410
(5d)	$(BuO)_8 H_2 Pc$	Toluene	738 (1.13)	761 (1.34)	13 550	13 140	410
(5e)	$(PentylO)_8 H_2 Pc$	Toluene	738 (1.20)	762 (1.39)	13 550	13 120	430
(5h)	$(OctylO)_8 H_2 Pc$	Toluene	740 (1.22)	762 (1.42)	13 510	13 120	390
		$CH_2 Cl_2$		767 (1.38)			
(5k)	$(DodecylO)_8 H_2 Pc$	$CH_2 Cl_2$		768 (1.45)			
(6d)	$(OctylO)_8 CuPc$	$CH_2 Cl_2$		752 (1.91)			
(7)	$(PentylO)_8 ZnPc$	$CH_2 Cl_2$		748 (1.32)			
(8)	$(PentylO)_8 NiPc$	Toluene		734 (1.66)			
		$CH_2 Cl_2$		742 (1.69)			

[a] Rhombic splitting $(Q_x - Q_y)$. [b] Material incompletely dissolved.

Table 6. Solubility of materials and $\lambda_{max.}$ for the Q-band absorption in nematic liquid crystal E7[a] at 20 °C

No.	Abbreviation	Solubility % (w/w)	$\lambda_{max.}/nm$
A[b]	$(Cl \cdot EtO/MeO)_8 H_2 Pc$	0.1	746
(1e)	$(Cl \cdot PentylO)_8 H_2 Pc$	0.4	762
(2)	$(Cl \cdot PentylO)_8 CuPc$	2.7	754
F[b]	$(BuO/MeO)_8 H_2 NPc$	0.2	866
(3d)	$(PentylO)_8 H_2 NPc$	0.3	871
(3e)	$(OctylO)_8 H_2 NPc$	0.1	874
(5e)	$(PentylO)_8 H_2 Pc$	1.3	770
(5h)	$(OctylO)_8 H_2 Pc$	2.5	771
(5k)	$(DodecylO)_8 H_2 Pc$	1.7	771
(6d)	$(OctylO)_8 CuPc$	1.5	759
(7)	$(PentylO)_8 ZnPc$	1.1	751
(8)	$(PentylO)_8 NiPc$	1.8	748

[a] E7 Is a formulation of cyanobiphenyls and cyanoterphenyls supplied by BDH Chemicals, Poole, Dorset, U.K. [b] Identifying letter refers to the product of that entry in Table 2.

Table 2. The solubilities at 20 °C, expressed as a percentage by weight of E7, are given in Table 6. Solubilities are in the range 0.1—2.5% (w/w). Members of the octa-alkoxy Pc series (5)—(8) are the most soluble of the materials examined. There are fluctuations with chain-length and the highest solubility of those investigated was recorded for the octa-octyloxy derivative (5h). The Q-band absorption in each series undergoes a small bathochromic shift in the liquid crystal medium relative to toluene.

From the point of view of the application in mind the modest solubility is largely offset by the advantageously high extinction coefficient of the Q-band. Thus the 1.3% (w/w) solution of the $(C_5 H_{11} O)_8 H_2 Pc$ (5e) in E7 has an absorbance of 1.7 at $\lambda_{max.}$ 770 in a 12 μm film aligned homeotropically (director orthogonal to plate) using a chrome complex agent. The absorbance minimum in the visible is less than 0.1. Under the same conditions, even the 0.2% solution of the product of entry F, Table 2, shows an absorbance of 0.6 at 850 nm.

The combination of strong near- i.r. absorbance and good transmission in the visible region, which are characteristics of the dyes examined in this study, is excellent for exploitation in a liquid crystal display addressed thermally using a semiconductor laser.

Conclusions

There is considerable scope for tuning the Q-band absorption of the Pc and NPc ring system to wavelengths in the far red and near- i.r. region of the spectrum. This can be achieved through the introduction of eight alkoxy groups at the benzenoid rings at sites α to the point of benzo-fusion to the heterocyclic rings. Comparison of the $(Cl \cdot RO)_8 H_2 Pcs$ and the $(RO)_8 H_2 Pcs$ shows that the presence of the chlorine atom at the 4,5-positions causes a small blue shift. The Q-band absorptions in these Pc derivatives varies between 711 and 736 to 740 and 762 nm in toluene solution. $(RO)_8 H_2 NPcs$ Absorb at 862 nm in toluene solution. Introduction of metal ions into the centre of both the Pc and NPc ring system offers a means of finer tuning of the wavelengths. All but the shortest alkoxy chain derivatives show good solubility in toluene, xylene, chloroform, and methylene dichloride and between ca. 0.1 and 2.5% (w/w) solubility at 20 °C in nematic liquid crystal E7.

Experimental

Materials.—The following were prepared by literature routes: 2,3-dichloro-5,6-dicyanohydroquinone (12) (97%), m.p. 290 °C (lit.,[12] >300 °C) by sodium metabisulphite reduction of the corresponding quinone, 2,3-dicyanonaphthalene-1,4-diol (13) (62%), m.p. >300 °C (lit.,[6] 300 °C) from 2,3-dichloro-1,4-naphthoquinone and KCN.[6,13] 2,3-Dicyanohydroquinone (14) was obtained from a commercial source (Aldrich Chemical Co. Ltd.).

Alkylations.—*Procedure* (a) *using diazomethane.* In a typical reaction, 2,3-dichloro-5,6-dicyanohydroquinone (12) (15 g) was suspended in ether (150 ml) and the mixture cooled to the temperature of an ice–salt bath. A solution of diazomethane (6 g) in ether was added with stirring over 15 min after which the mixture was evaporated to dryness (rotary evaporator/fume hood). The residue was recrystallised from ethanol to afford 4,5-

dichloro-3,6-dimethoxyphthalonitrile (9a) (11.2 g, 67%), m.p. 187 °C (lit.,[6] 189 °C).

Procedure (b) *using alkyl halides*. In a typical experiment, 2,3-dicyanonaphthalene-1,4-diol (13) (1.0 g, 4.8 × 10^{-3} mol), ethyl iodide (3.7 g, 2.4 × 10^{-2} mol), and anhydrous potassium carbonate (3 g) in anhydrous acetone (75 ml) were heated under reflux for 60 h. The mixture was filtered whilst hot and the residue washed with warm acetone (2 × 50 ml). The washings were combined with the reaction solution and the whole evaporated to dryness. The residue was recrystallised from acetone to afford 1,4-*diethoxynaphthalene*-2,3-*dicarbonitrile* (10b) (0.25 g, 40%), m.p. 169—171 °C as light tan needles.

Table 1 summarises yields and combustion analysis data for 20 compounds prepared by the above procedures. Two more derivatives, 4,5-dichloro-3,6-dipentyloxyphthalonitrile (9e) (58%), m.p. 46—48 °C, $v_{max.}$(thin film) 3 050—2 800 (CH), 2 230 (C≡N), 1 240 and 1 050 cm^{-1} (C–O–C), and 3,6-dioctyloxyphthalonitrile (11h) (51%), m.p. 147 °C, $v_{max.}$(thin film) 3 075 (CH aromatic), 2 920 (CH aliphatic), 2 220 (C≡N), 1 275 and 1 050 cm^{-1} (C–O–C), were used in the next step without purification.

Metal-free Phthalocyanine and Naphthalocyanine Derivatives (Tables 2 and 3).—Procedure (c). In a typical experiment, a modification of the method of Witkiewicz *et al.*,[5] lithium metal (0.75 g) was added to a refluxing solution of 3,6-diethoxyphthalonitrile (1.0 g, 4.6 × 10^{-3} mol) in pentanol (10 ml) under a nitrogen atmosphere. The reaction solution was maintained at reflux for 0.75 g, cooled, and stirred into glacial acetic acid (100 ml). After 0.25 h, the bulk of the solvent was removed and the green residue dissolved in dichloromethane (50 ml). The solution was washed with 10% hydrochloric acid (100 ml) and brine (100 ml) and the organic phase separated, dried ($MgSO_4$), and evaporated. The residue was chromatographed (silica gel, CH_2Cl_2 and ether as eluants) and the green fraction recrystallised from a slowly evaporating solution in CH_2Cl_2–pyridine (95:5) to yield *metal-free* 1,4,8,11,15,18,22,25-*octaethoxyphthalocyanine* (0.2 g, 20%), m.p. >300 °C.

Procedure (d). In a modification of the above procedure, a solution of 1.5M butyl-lithium (0.64 g, 0.01 mol) in THF was added under nitrogen to a stirred solution of octanol (5 g, 38 mmol) at room temperature. The temperature was raised to 145—150 °C and 1,4-dioctyloxynaphthalene-2,3-dicarbonitrile (0.5 g, 1.15 × 10^{-3} mol) was added. The reaction was heated for a further 1 h, cooled and worked-up as above to yield *metal-free* 1,6,10,15,19,24,28,33-*octaoctyloxynaphthalocyanine* (0.075 g, 15%), m.p. 148 °C.

Metal phthalocyanine and naphthalocyanine derivatives (Table 4). Procedure (e). In a typical reaction copper(II) acetate monohydrate (0.75 g, 3.7 × 10^{-3} mol) was added to a refluxing solution of metal-free 1,4,8,11,15,18,22,25-octapropyloxyphthalocyanine (0.1 g, 1.02 × 10^{-4} mol) in butan-1-ol (5 ml). The solution was maintained at reflux for 0.5 g, cooled, and chromatographed (silica gel, CH_2Cl_2 and ether as eluants). The green-blue fraction eluted first was crystallised from a slowly evaporating solution in CH_2Cl_2–pyridine to afford the *copper analogue* (0.086 g, 81%), m.p. >300 °C.

Spectroscopy.—U.v.–visible spectra were measured for solutions in spectroscopic grade toluene or Aristar grade

chloroform using either a Pye-Unicam SP8-200 or a Cary 17D UV-Visible spectrometer. Fluorescence spectra of compounds (1a) and (3d) were measured using a home-built spectrofluorimeter described elsewhere[14] and corrected by standard procedures.[14] The fluorescence spectrum of compound (5e) was measured at the Royal Institution, London using a Perkin-Elmer MPF4 fluorescence spectrometer fitted with a Hitachi R446 photo-multiplier. The spectrum was uncorrected.

Solubility of Pcs in Liquid Crystals.—The dye (2—10 mg) was added to the liquid crystal E7 (200—250 mg) (B.D.H. Ltd. Poole) and the mixture stirred (Denley Spiramix) at room temperature for a continuous period of at least 2 weeks. An excess of the dye was maintained during this period. The resultant mixture was filtered (Millipore, pore size 0.2 μm) and a known weight of the filtrate (10—20 mg) was dissolved in either Spectrosol grade chloroform or Aristar grade dichloromethane (10—25 ml). The absorption spectra of the solution and that of a standard solution (*ca.* 10^{-6} molar) of the dye in Spectroscol grade chloroform were recorded (Perkin-Elmer Lambda 9 UV/Vis./Near IR spectrophotometer). The absorbance of the solutions at their wavelength maxima were used to calculate the solubility of the dye in the liquid crystal E7 at room temperature.

References

1 M. Whalley, *J. Chem. Soc.*, 1961, 866.
2 *e.g.* (*a*) S. A. Mikhalenko and E. A. Luk'yanets, *Zh. Obshch. Khim.*, 1969, **39**, 2129; (*b*) S. A. Mikhalenko, E. A. Korobkova, and E. A. Luk'yanets, *ibid.*, 1970, **40**, 400; (*c*) P. J. Duggan and G. P. Francis, *Eur. Pat. Appl.* EP 1565,780 (25 Sept., 1985, *Chem. Abstr.*, 1986, **105**, 70242r).
3 S. A. Mikhalenko and E. A. Luk'yanets, *Zh. Obshch. Khim.*, 1969, **39**, 2554.
4 N. B. McKeown, Ph.D. Thesis, University of East Anglia, Norwich, 1987.
5 Z. Witkiewicz, R. Dabrowski, and W. Waclawek, *Material Science*, 1978, **11**, 39.
6 K. Wallenfels, G. Bachmann, D. Hofmann, and R. Kern, *Tetrahedron*, 1965, **21**, 2239.
7 A. B. P. Lever, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 27.
8 L. E. Lyons, J. R. Walsh, and J. W. White, *J. Chem. Soc.*, 1960, 167.
9 A. R. Koray, V. Ahsen, and O. Bekoroglu, *J. Chem. Soc., Chem. Commun.*, 1986, 932.
10 E. A. Cuellar and T. J. Marks, *Inorg. Chem.*, 1981, **20**, 3766.
11 P. J. Duggan and G. P. Francis, *Eur. Pat. Appl.*, EP 155 780, 25 Sept. 1985 (*Chem. Abstr.*, **105**, 70242r).
12 P. W. D. Mitchell, *Can. J. Chem.*, 1973, **41**, 550.
13 G. A. Reynolds and J. A. Van Allen, *J. Org. Chem.*, 1964, **29**, 3591.
14 M. J. Cook, A. P. Lewis, G. S. G. McAuliffe, V. Skarda, A. J. Thomson, J. L. Glasper, and D. J. Robbins, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1293.