

Binuclear phthalocyanines covalently linked through two- and four-atom bridges¹

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Binuclear phthalocyanines in which the two phthalocyanine nuclei are covalently linked through four-atom bridges, derived from catechol, have been prepared and characterized. Metal-free 2,9,16,23-tetra-(3,3-dimethylbutyl)phthalocyanine and 2,9,16,23-tetra-(2-trimethylsilylethyl)phthalocyanine were prepared as examples of non-oxygenated mononuclear phthalocyanines soluble in organic solvents. Catalytic hydrogenation of 1,2-bis-(3,4-dicyanophenyl)ethyne and 1,4-bis-(3,4-dicyanophenyl)buta-1,3-diyne gave 1,2-bis-(3,4-dicyanophenyl)ethane and 1,4-bis-(3,4-dicyanophenyl)butane respectively. From these precursors, metal-free phthalocyanine dimers containing ethylene and tetramethylene bridges, joining the phthalocyanine nuclei, were prepared. Two of the two-atom bridge phthalocyanine dimers represent the first characterized phthalocyanine dimers not containing alkoxy or oxygenated groups.

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On a préparé et on a caractérisé deux phthalocyanines binucléaires dans lesquelles deux noyaux phthalocyanines sont liés d'une façon covalente par quatre atomes de pont, dérivés du catéchol. On a préparé la tétra(diméthyl-3,3 butyl)-2,9,16,23 phthalocyanine et la tétra(triméthylsilyle-2 éthyle)-2,9,16,23 phthalocyanine exemptes de métal à titre d'exemples de phthalocyanines mononucléaires non oxygénées solubles dans des solvants organiques. Les hydrogénations catalytiques du bis(dicyano-3,4 phényl)-1,2 éthyne et du bis(dicyano-3,4 phényl)-1,4 butadiyne-1,3 conduisent respectivement au bis(dicyano-3,4 phényl)-1,2 éthane et au bis(dicyano-3,4 phényl)-1,4 butane. À l'aide de ces précurseurs, on a préparé des phthalocyanines dimères sans métal contenant des ponts éthylènes et tétraméthylène entre les noyaux phthalocyanines. Deux de ces phthalocyanines dimères correspondent aux premières phthalocyanines ne contenant pas de groupements alkoxy ou oxygénés à être caractérisées.

The electrocatalytic properties of porphyrins and phthalocyanines have been the subject of intensive research (1). A dicobalt cofacial porphyrin dimer (2, 3) containing a four-atom covalent bridge has been prepared. The four-electron reduction of oxygen to water using this dimer has been achieved but the compound tends to lose its catalytic activity with time (2). Since the phthalocyanine nucleus is likely to be more stable (4) than the porphyrin nucleus, we have tried to synthesize the related, but hitherto unknown, phthalocyanine dimers. We have recently reported the synthesis and some properties of phthalocyanine dimers incorporating five-atom covalent bridges (5, 6). Unlike typical phthalocyanines, these dimers are very soluble in organic solvents and their great solubility facilitates their purification and characterization. Recent work on the synthesis of porphyrin dimers has shown that even dimers having one rigid covalent bridge can be held in a cofacial conformation thought to be necessary for electrocatalysis (7). Since a four-electron reduction of oxygen was not achieved using the five-atom bridge dimer (5), we wished to prepare phthalocyanine dimers separated by the key four-atom bridges (2, 3) and to provide binuclear phthalocyanines containing two-atom bridges or less as control electrocatalysts that cannot assume a cofacial conformation. In addition, we wished to study the possibility of synthesizing binuclear phthalocyanines

devoid of alkoxy groups or any oxygen atoms. In this paper we describe the preparation of a partially constrained binuclear phthalocyanine, containing a four-atom covalent bridge derived from catechol units; a flexible tetramethylene four-atom bridged phthalocyanine dimer; and phthalocyanine dimers containing two-atom ethylene bridges.

Synthesis of binuclear phthalocyanines bridged covalently by catechol units

Treatment of 4-nitrophthalonitrile (1) with 4-*tert*-butylcatechol (2a) or catechol (2b) and anhydrous potassium carbonate in dry dimethylformamide (DMF) at 22°C for 36 h gave 1,2-bis-(3,4-dicyanophenoxy)-4-*tert*-butylbenzene (3a)³ and 1,2-bis-(3,4-dicyanophenoxy)benzene (3b)³ in 84 and 78% yields, respectively (9, 10). Compounds 3a,b were converted to their respective 1,3-diiminoisoindolines (4a,b) by bubbling ammonia into a solution of 3a or 3b and sodium methoxide in dry methanol under reflux for 6 h or until an infrared spectrum of an aliquot of the reaction mixture no longer exhibited the typical nitrile absorption peak (5, 6, 11, 12). Condensation (5, 6, 11, 12) of 4a with 5-neopentoxy-1,3-diiminoisoindoline (5) in 2-*N,N*-dimethylaminoethanol for 60 h gave a green-black solution, which was diluted with water to give a blue coloured residue. Flash chromatography (13) of the residue taken up in toluene yielded, in the first fractions using toluene as eluant, 2,9,16,23-tetraneopentoxyphthalocyanine (6) (5, 6) as a mix-

¹Presented in part at the 67th Chemical conference of the Chemical Institute of Canada, Montreal, Quebec, June 1984, Nos. IN5-5 and IN5-6.

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³See Table 1 for ¹³C chemical shift values. Standard correlation tables were used as an aid to assignments (8).

TABLE 1. ^{13}C nuclear magnetic resonance chemical shifts in ppm (δ) of some phthalonitriles and bis-phthalonitriles

Carbon ^a	Compound									
	3a ^b	3b	9	12	13	14	15	29	30	32
1	109.4	109.9	113.8	115.0	115.2	112.5	112.1	115.2	112.4	114.0
2	117.6	—	116.8	116.0	115.8	115.5	115.1	114.2	115.2	114.2
3	120.8 ^c	120.8 ^c	141.9	135.9	135.6	132.7	133.1	136.2	132.7	133.8
4	160.7	160.4	99.7	128.9	130.1	151.9	150.1	128.0	150.6	149.2
5	120.6 ^c	120.6 ^c	142.4	136.2	135.9	133.3	122.6	136.5	133.3	134.2
6	135.5	135.5	133.9	133.3	133.2	132.8	133.6	133.5	132.8	134.0
7	115.2 ^d	115.1 ^d	114.9 ^c	114.6 ^c	113.6 ^c	115.5	115.2 ^c	114.5 ^c	115.4 ^c	116.1 ^c
8	114.9 ^d	114.7 ^d	114.9 ^c	114.4 ^c	114.8 ^c	115.5	115.3 ^c	114.8 ^c	115.4 ^c	116.6 ^c
9	144.1	144.9	—	103.2	106.7	30.0	44.8	84.4	28.4	36.0
10	142.1	144.9	—	100.5	76.4	17.9	30.8	79.7	14.3	30.6
11	123.0	123.7	—	—	28.1	—	30.0	—	—	—
12	125.6	128.6	—	-0.6	30.4	-2.0	28.7	—	—	—
13	152.8	128.6	—	—	—	—	—	—	—	—
14	120.6 ^c	123.7	—	—	—	—	—	—	—	—

^aThe numbering of the carbon atoms in the compounds listed follows that given for these structures in the schemes and does not follow from the names of the compounds.

^bThe chemical shift values for the *tert*-butyl group are 34.9 and 31.1 ppm for the quaternary and methyl groups respectively.

^cThese values may be interchanged.

^dThese values may be interchanged.

TABLE 2. Absorption spectra of mononuclear and binuclear phthalocyanines (pc) and their solubilities in CH_2Cl_2^a

Pc	λ_{max} (nm) (ϵ log)						Solubility (mol/L)
7a	708 (4.88)	676 (4.92)	642 (4.84)	620 (4.75)	388 (4.63)	336 (4.98)	^b
7b	698 (4.83)	666 (4.93)	638 (4.94)	618 (4.84)	384 (4.67)	334 (5.08)	0.1
7c	—	672 (4.97)	—	628 (4.90)	326 (4.91)	290 (5.03)	0.06
18	698 (5.25)	664 (5.19)	644 (4.81)	604 (4.59)	342 (5.02)	292 (4.76)	0.7
19	698 (5.11)	664 (5.05)	644 (4.67)	604 (4.45)	342 (4.88)	290 (4.58)	0.1
20 ^c	—	672 (5.04)	—	608 (4.45)	330 (4.75)	290 (4.72)	<10 ⁻⁵
25 ^c	702 (4.86)	668 (4.92)	642 (4.90)	620 (4.83)	340 (5.08)	292 (4.81)	<10 ⁻⁶
26 ^c	702 (4.93)	666 (4.96)	644 (4.90)	618 (4.81)	340 (5.10)	292 (4.85)	<10 ⁻⁶
27 ^d	706 (4.98)	672 (5.03)	646 (4.96)	620 (4.86)	344 (5.05)	296 (4.79)	<10 ⁻⁵
28 ^d	—	680 (4.99)	—	626 (4.69)	336 (4.87)	296 (5.02)	<10 ⁻⁵
34 ^d	708 (4.94)	672 (5.02)	644 (4.99)	620 (4.87)	342 (5.09)	296 (5.02)	<10 ⁻⁵

^aSolubilities were determined at 24°C by visible spectroscopy of saturated solutions in CH_2Cl_2 .

^bAvailable small quantities of 7a were insufficient to obtain reliable data on this very soluble dimer.

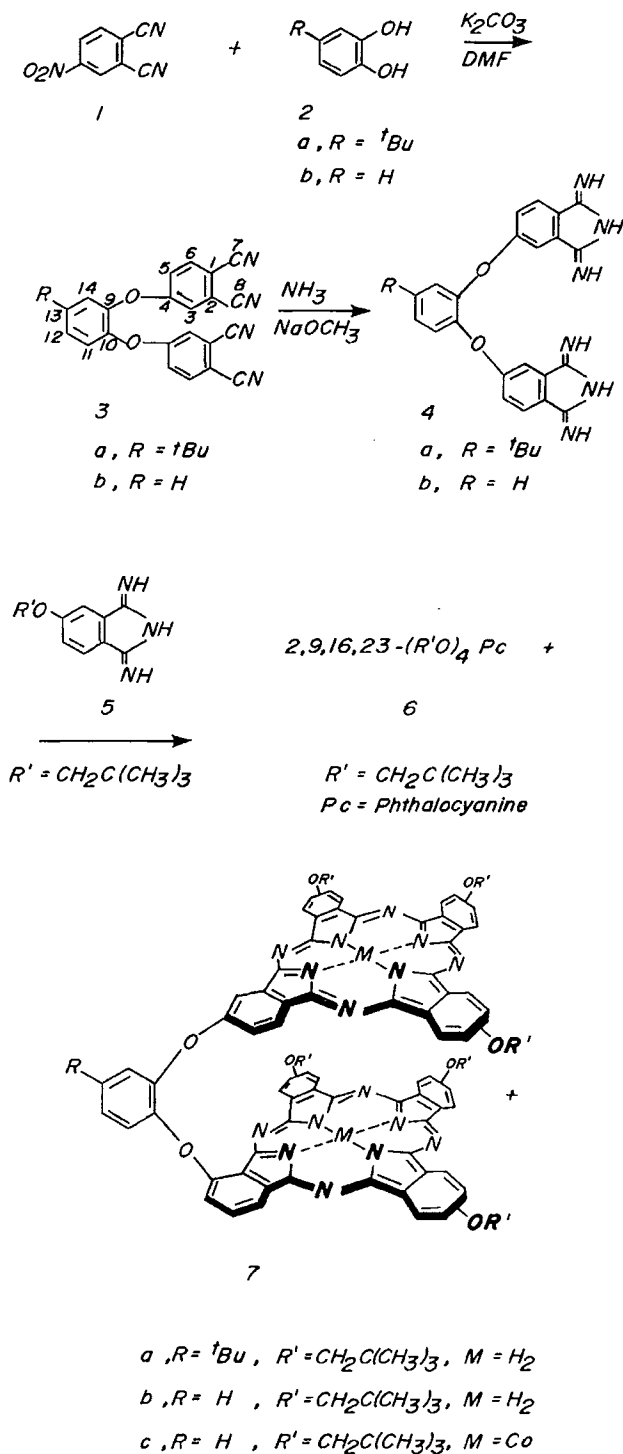
^cThese absorption spectra were taken in CHCl_3 .

^dThese absorption spectra were taken in *o*-dichlorobenzene.

ture of isomers. Further elution with toluene gave mixtures of **6** and 1,2-bis-2'-(9',16',23'-trineopentoxypthalocyaninoxy)-4-*tert*-butylbenzene (**7a**) and some later fractions of pure **7a** as shining dark purple plates.⁴ Repetitive flash chromatography of the mixed fractions **6** and **7a** gave pure **7a** in 13% overall yield (Scheme 1). We initially selected 4-*tert*-butylcatechol (**2a**) as the bridging moiety of binuclear phthalocyanines so that the resultant phthalocyanine dimer would be soluble in organic solvents. This idea was realized but **7a** was actually too mobile chromatographically so that separation from the monomer **6** was tedious. The above synthesis was subsequently repeated but using catechol (**2b**) as the bridging group. Thus, the 1,3-diminoisoindoline (**4b**) was condensed with **5** as before. Flash

⁴Continued elution with toluene and toluene/2-methoxyethanol mixtures gave an additional blue-green fraction which, by fast atom bombardment analysis (FAB) (14), was shown to have a molecular ion corresponding to a phthalocyanine trimer.

chromatography (13) of the resultant blue-green mixture was much more facile, as monomer **6** eluted first in toluene, followed by mixed monomer-dimer fractions using toluene and toluene/2-methoxyethanol (50:1) as eluants.⁴ Rechromatography of the mixed fractions gave pure 1,2-bis-2'-(9',16',23'-trineopentoxypthalocyaninoxy)benzene (**7b**) in 10% yield. Phthalocyanine dimer **7b** was readily converted to its dicobalt(II) derivative **7c** by heating **7b** with CoCl_2 in toluene at 110°C for 30 h. Dimer **7c** was purified as before by flash chromatography using toluene/2-methoxyethanol (50:1) as eluant. The structures of **3a,b** and **7a-c** have been fully characterized by spectroscopic data and elemental analysis (see Experimental). The absorption spectra of **7a-c** are characteristic of metal-free and metallophthalocyanine dimers respectively (6) (Table 2). Most importantly, the fast atom bombardment (14) (FAB) mass spectra of the binuclear phthalocyanines **7a-c** all exhibit parent ion clusters almost identical in intensity to those calculated for their respective isotopic compositions. It



SCHEME 1

should be noted, however, that phthalocyanines **7a–c** exist as a mixture of positional isomers about the phthalocyanine ring and that the depicted structure thus reflects this mixture. The broad absorbances in the ^1H nmr spectra of these compounds are indicative of this isomeric distribution (Table 3). On the other hand, the ^{13}C nmr spectra of **7a** and **7b** exhibit single resonances for the methyl and quaternary carbon groups of the neopentoxy substituents. Thus ^{13}C nmr spectra of **7a,b** are diagnostic concerning their skeletal structure (Table 4), while

the ^1H nmr spectra clearly identify the internal NH protons of **7a, b** (Table 3).

Synthesis of 2,9,16,23-tetraalkylphthalocyanines

It has been shown (15, 16) that a wide variety of alkynes can couple with iodoarenes even at room temperature using cuprous iodide and bis(triphenylphosphine)palladium dichloride. We believed that this reaction could provide the basis for preparing the 4-alkylphthalonitriles and bisphthalonitriles needed for the preparation of mono and binuclear phthalocyanines containing no alkoxy substituents or oxygen atoms in the bridges of the phthalocyanines.

Catalytic hydrogenation of **1** in ethanol using 10% palladium on charcoal yielded 4-aminophthalonitrile (**8**) in 84% yield. Diazotization of **8** and subsequent reaction of the first-formed diazonium salt with potassium iodide gave 4-iodophthalonitrile (**9**)³ in high yield. Coupling of **9** with trimethylsilylacetylene (**10**) (16) or 3,3-dimethyl-1-butyne (**11**) (15, 16) gave 4-(2-trimethylsilylethynyl)phthalonitrile (**12**)³ or 4-(3,3-dimethyl-1-butynyl)phthalonitrile (**13**)³ in 75% and 75% yield, respectively. Hydrogenation of **12** and **13** using palladium on charcoal as a catalyst gave the corresponding 4-alkyl derivatives, 4-(2-trimethylsilylethyl)phthalonitrile (**14**)³ and 4-(3,3-dimethylbutyl)phthalonitrile (**15**)³ in high yield. Conversion of **14** and **15** to their 1,3-diiminoisoindolines (**16**) and (**17**) as before (5, 6, 11, 12) and subsequent self-condensation in 2-*N,N*-dimethylaminoethanol gave 2,9,16,23-tetra-(2-trimethylsilylethyl)-phthalocyanine (**18**) and 2,9,16,23-tetra-(3,3-dimethylbutyl)-phthalocyanine (**19**) in 28% and 40% yields, respectively (Scheme 2). Phthalocyanine (**19**) was readily converted to its cobalt(II) derivative (**20**) as before (6, 11).

The mass spectra of **18–20** exhibited parent ions using the FAB technique (14). The ^1H nmr spectra of **18** and **19** were most informative and showed the inner NH absorptions (Table 3). In addition, the trimethylsilyl group of **18** and the *tert*-butyl group of **19** showed four and six peaks, respectively, corresponding to the eight different environments that these groups may experience in the four isomers possible for a tetrasubstituted phthalocyanine containing one substituent on each benzene ring. For 2,9,16,23-tetra-*tert*-butylphthalocyanine (**6**), the *tert*-butyl group gave an unresolved broad absorption peak in its ^1H nmr spectrum when recorded at high concentrations (6) but also exhibited 6 individual absorption peaks at lower concentrations (Table 3).

The ^{13}C nmr spectra of **18** and **19** exhibited only two peaks for the trimethyl group and the *tert*-butyl group while **6** showed only a single peak. On the other hand the $-\text{SiCH}_2-$ group and $-\text{Si}-\text{CH}_2\text{CH}_2-$ groups exhibited 8 and 6 peaks, respectively, indicating that all four isomers of **18** were indeed present (Table 4). Comparison of the solubilities of **18** and **19** with **6** showed that the tetraalkylphthalocyanines were less soluble than the tetraalkoxyphthalocyanine (**6**) (Table 2). The absorption spectra of **18** and **19** were consistent with the assigned structures (Table 2) (**6**).

Preparation of binuclear phthalocyanines covalently linked by dimethylene bridges

The dicoupling (15) of an acetylene to an iodoarene should provide the unknown bisphthalonitriles necessary to form binuclear phthalocyanines containing an all-carbon bridging group.

Thus treatment of 4-iodophthalonitrile (**9**) by methods previously described with acetylene (**21**) gave 1,2-bis-(3,4-dicyanophenyl)ethyne (**22**) in 90% yield. Compound **22** was very

TABLE 3. ¹H nuclear magnetic resonance chemical shifts in ppm (δ) of some mononuclear and binuclear phthalocyanines (Pc)

Pc	Solvent	Concentration (M)	Temperature (°C)	Proton type				
				Aromatic	CH ₂ X	CH ₂ Pc	(CH ₃) ₂ Z	NH
6 ^a	CD ₂ Cl ₂	10 ⁻¹	22	7.6-6.0(m)	3.8(br s)	—	1.5(s)	-6.5
6 ^b	CD ₂ Cl ₂	10 ⁻⁴	-70	c	4.3-3.7(br)	—	1.4(br), 1.2, 1.1, 0.9(br)	-3.1(br)
6 ^{b,d}	CDCl ₃	10 ^{-4u}	50	c	4.23, 4.22, 4.20, 4.19	—	1.09, 1.08, 0.88, 0.86, 0.85, 0.83	-1 to -3(v br)
6	C ₇ D ₈ ^e	10 ⁻⁴	-80	c	4.5-3.5(br)	—	1.2(br), 0.1(br)	-0.9(br)
6	C ₇ D ₈ ^e	10 ⁻⁴	22	c	3.9, 3.8	—	1.7(br), 1.3(br), 1.0(br), 0.5(br)	-2.6(v br)
6	C ₇ D ₈ ^e	10 ⁻⁴	80	c	4.0, 3.9	—	1.4, 1.2, 1.1	-3.0(v br)
6Zn ^g	CD ₂ Cl ₂	10 ⁻¹	22	7.7-6.1(m)	3.5(s)	—	1.3(s)	—
6Zn	CDCl ₃	10 ⁻³	22	8.2-6.4(br)	4.04, 4.01, 3.95, 3.82, 3.74, 3.72, 3.70	—	1.38, 1.37, 1.35, 1.34, 1.31, 1.25, 1.06	—
18	CDCl ₃	2 × 10 ⁻³	22	8.7-7.4(br)	1.25(t)	3.10(t)	0.32, 0.31, 0.30, 0.29	-2.9(br)
19	CDCl ₃	10 ⁻³	22	8.7-7.4(br)	1.88(t)	3.01(t)	1.28, 1.27, 1.24, 1.23, 1.225, 1.22	-3.2(br)
7a	CDCl ₃	10 ⁻¹	22	c	4.4-3.6(br)	—	1.8-0.9(m)	-6.0(br)
7b	CDCl ₃	10 ⁻³	22	c	4.2-3.3(br)	—	1.5-0.8(m)	-3.1(br)
7b	CDCl ₃	10 ⁻³	50	c	4.4-3.3(br)	—	1.4-0.8(m)	-3.3(br)
7b	CD ₂ Cl ₂	10 ⁻⁴	-70	c	4.7-3.8(br)	—	1.6-0.9(m)	-3.0(br)
25	CDCl ₃	10 ⁻³	22	c	0.8-(-0.6)	3.5(br)	0.8-(-0.6)	-1 to -3(v br)
26	CDCl ₃	10 ⁻³	22	c	1.3-0.8	3.5(br)	1.3-0.8	-1 to -3(v br)
27	CDCl ₃	10 ⁻³	22	c	4.1-3.4(br)	—	1.3-0.7(br)	-1 to -3(v br)
34	CDCl ₃	10 ⁻³	22	c	4.1-3.5(br)	—	1.4-0.8(m)	-1 to -3(v br)
35	CDCl ₃	10 ⁻⁴	22	c	4.2-3.6(br)	—	1.5-0.9(m)	-1 to -3(v br)
35	CDCl ₃	10 ⁻⁴	50	c	4.2-3.2(br)	—	1.5-0.8(m)	-3.2(br)
35	CD ₂ Cl ₂	10 ⁻⁴	-70	c	3.9-3.1(br)	—	1.4-0.8(m)	-2.8(br)

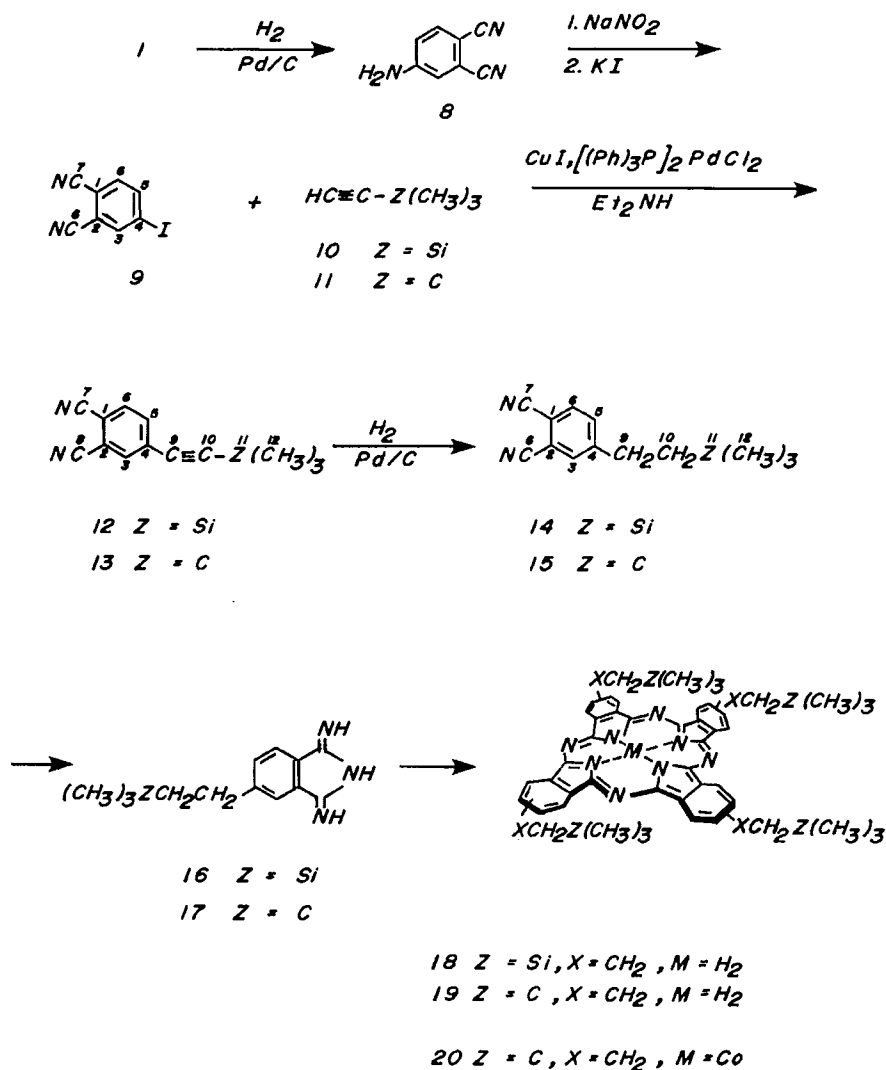
^aThese data were taken from ref. 6. A Bruker WH250 instrument was used to record this spectrum.

^bThese measurements were done on a Bruker WH400 instrument.

^cThe absorptions in this region were very weak.

^dThe absorption of the NH protons was studied in CDCl₃ at 10⁻¹, 10⁻², 10⁻³, 10⁻⁴, and 10⁻⁵ M concentrations and gave values of -5.5(br), -3.0(v br) and 4.1(br), -3.0(br), and -3.0(br), respectively.

^eToluene-d₈.



SCHEME 2

insoluble in most solvents except acetonitrile. Thus a suspension of **22** in acetonitrile was hydrogenated for 4 h at room temperature with shaking over 10% palladium on charcoal to give, in 83% yield, 1,2-bis-(3,4-dicyanophenyl)ethane (**23**). Compound **23** was converted to its 1,3-diiminoisoindoline (**24**) as before (5, 6, 11, 12) and condensed with an excess of the 1,3-diiminoisoindolines **16**, **17**, or **5** to give, after chromatographic separation, large amounts of the mononuclear phthalocyanines **18**, **19**, or **6** and 7–10% yields of 1,2-bis-2'-(9',-16',23'-tri-(2-trimethylsilylethyl)phthalocyaninyl)ethane (**25**), 1,2-bis-2'-(9',16',23'-tri-(3,3-dimethylbutyl)phthalocyaninyl)ethane (**26**) and 1,2-bis-2'-(9',16',23'-trineopentoxylphthalocyaninyl)ethane (**27**), respectively. Metal-free phthalocyanine **27** was readily converted to its dicobalt(II) derivative (**28**) (6, 11) (Scheme 3).

Binuclear phthalocyanines **25**–**27** exhibited the typical absorption spectra of metal-free binuclear phthalocyanines (**6**) while **28** exhibited the typical absorption of a metalated phthalocyanine dimer (Table 2). Compounds **25**–**28** all exhibited parent ions in their mass spectra using the FAB technique (14). Phthalocyanine dimers **25**–**28** were very much less soluble in organic solvents than the four-atom bridged catechol type

dimers described above and the previously described five-atom bridged dimers (Table 2). The ^1H nmr of **25**–**27** were taken in dilute solutions and exhibited broad absorptions at the appropriate peak positions for the substituent groups (Table 3). The ^1H nmr spectra of the inner NH protons of **18**, **19**, and **6** are dependent on concentration, solvent, and temperature (Table 3). As a result of our initial examination of these effects on the ^1H nmr of **6** (Table 3), we generally run our samples in CDCl_3 or toluene- d_8 (C_7D_8) at concentrations of 10^{-3} to 10^{-4} M at room temperature. The effects of concentration, solvent, and temperature on porphyrin monomers and dimers have been studied and the effects noted here are consistent with those trends noted in porphyrin chemistry (17, 18).

Preparation of a binuclear phthalocyanine covalently linked by a tetramethylene bridge

As has been shown above in the preparation of **18**, 4-iodophthalonitrile (**9**) can readily couple with trimethylsilylethyne (**10**) to give **12**. Attempts to hydrolyze **12** as before (**16**) or by alternate procedures (**19**) resulted in solutions from which the desired 4-ethynylphthalonitrile (**29**)³ could only be isolated in low yield. Hydrolysis of **12** under very mild conditions did

TABLE 4. ^{13}C nuclear magnetic resonance chemical shifts in ppm (δ) of some saturated solutions of mononuclear and binuclear phthalocyanines (Pc) in CDCl_3 at 22°C

Pc	Carbon type				
	Aromatic	CH_2X^a	CH_2Pc	C'Bu	$(\text{CH}_3)_3\text{Z}^b$
6 ^c	160.6, 122.1, 117.4, 117.2	78.6, 78.4	—	32.5	27.3
6Zn ^c	160.1, 149.5, 121.7, 121.3, 116.9, 116.6, 104.2, 103.9	78.2, 78.1	—	32.2	27.1, 26.8, 26.5
18	147.4(m), 146.3(m), 132.9(m), 128.3(m), 120.4(m)	19.3, 19.2, 19.1, 19.0, 18.9, 18.8, 18.7, 18.5	31.0, 30.95, 30.8, 30.7, 30.5, 29.4	—	-1.35, -1.4
19	128.5, 120.4	30.8, 30.7	46.6	31.6, 31.5	29.7, 29.6
7a ^{d,e}	160.9	78.5	—	32.2	27.1
7b	f	78.2	—	32.1	27.1, 27.0, 26.5
25	145.5, 130.2, 120.9 ^f	18.9	31.3, 29.7	—	-1.4, -1.5, -1.7
26	f	f	f	f	29.7
27	f	77.2	—	31.9	26.9
34 ^g	—	77.8, 77.3	36.2	32.2, 32.15	27.4, 27.2
35 ^{c,h}	f	78.6	f	32.4	27.2

^aX = O for all compounds except 18, 19, 25, and 26 where X = CH_2 .

^bZ = C for all compounds except 18 and 25 where Z = Si.

^cThese data were taken from ref. 6.

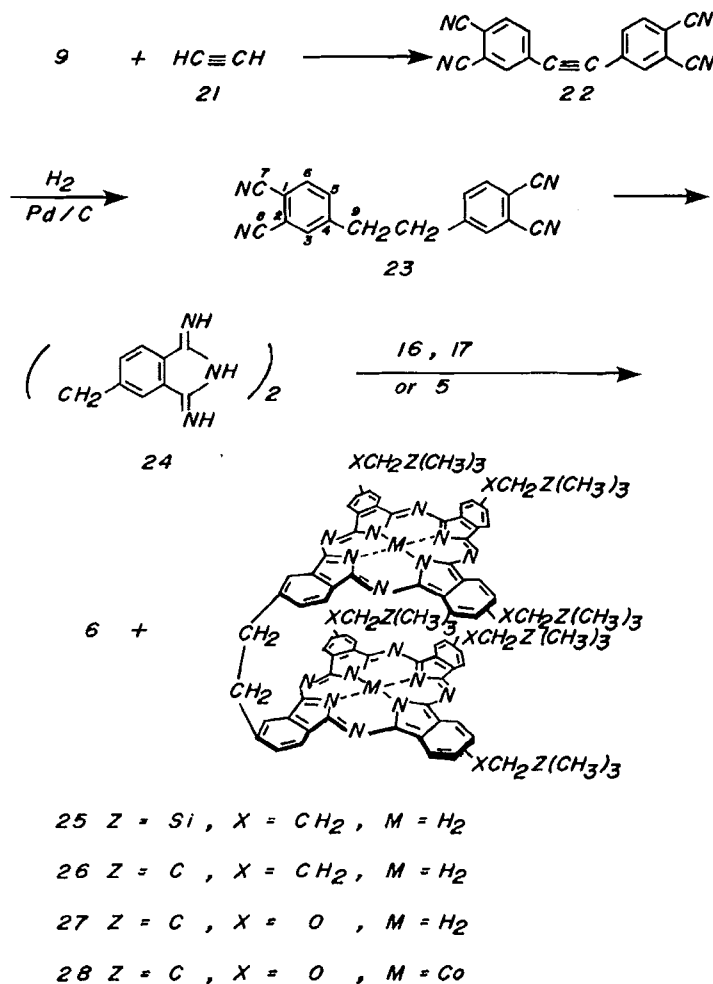
^dWeak absorptions at 31.8 and 26.5 are likely due to the bridging *tert*-butyl group.

^eThis measurement was done on a Bruker WH400 instrument.

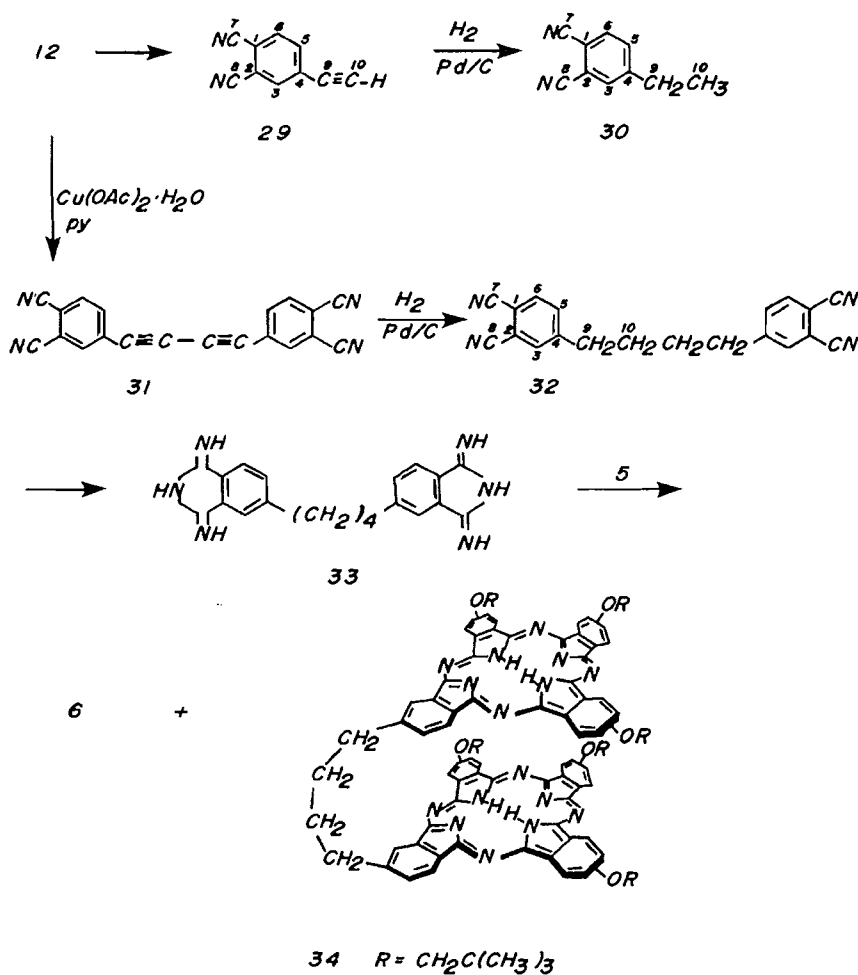
^fThe absorptions in this region were very weak.

^gWeak absorptions at 26.8, 26.73, 26.7, and 26.6 are likely due to bridging carbons.

^hWeak absorptions at 30.1 and 26.6 ppm are likely due to bridging carbons.



SCHEME 3



SCHEME 4

proceed in methanolic pyridine or in pyridine-Cu(OAc)₂ at room temperature to give **29** in high yield. Hydrogenation of **29** afforded 4-ethylphthalonitrile (**30**).³ Since we wished to perform an oxidative dimerization (**20**, **21**) of **29** to give 1,4-bis-(3,4-dicyanophenyl)-1,3-butadiyne (**31**) and since the conditions of this dimerization (Cu(OAc)₂, pyridine, methanol) are the very conditions that promote the hydrolysis of **12** to **29**, we felt that direct coupling of the precursor to **29**, i.e. **12**, should give the desired product **31**. Indeed, oxidative coupling of **12** yielded **31** in 76% yield. Catalytic hydrogenation of **31** as before gave 1,4-bis-(3,4-dicyanophenyl)butane (**32**)³ in high yield. Conversion of **32** into its bis-1,3-diiminoisoindoline (**33**) as before (**5**, **6**) and subsequent mixed condensation with **5** gave the undesired monomer **6** and the tetramethylene bridged dimer 1,4-bis-2'-(9',16',23'-trineopentoxypthalocyaninyl)-butane (**34**) in 1.4% yield (Scheme 4).

Physical and spectroscopic properties of mononuclear and binuclear phthalocyanines

We have shown (**6**) that binuclear metal-free and metallophthalocyanine exhibit characteristic absorption spectra differing from each other and from the well-known absorption spectra of mononuclear metal-free and metallophthalocyanines (**4**). Thus, the mononuclear phthalocyanines **18**–**20** exhibit the characteristic absorptions (Table 2) of monomers, while binuclear phthalocyanines **7a**–**c**, **25**–**28**, and **34** all exhibit ab-

sorptions more typical of dimeric phthalocyanines.

The visible spectra of **7a**, **b**, **25**–**27**, and **34** show double π - π^* bands near 700 and 670 nm, but the bands near 640 and 620 nm exhibit enhanced intensities compared to the model monomers **6**, **18**, and **19**. In addition, compounds **7c** and **28** exhibit bands at 680 and 620 nm similar to the cobalt(II) derivative of **6** (**5**) and **20**, but the intensity of the band at 620 is greatly enhanced, typical of aggregation (**22**, **23**). Thus, the visible spectra of **7a**–**c**, **25**–**28**, and **34** indicate substantial interaction between the phthalocyanine nuclei. This interaction is intramolecular rather than intermolecular since the blue shift is unaffected by dilutions in the range of 10^{-5} – 10^{-6} M. A full description of the absorption and emission spectra of mononuclear and binuclear metal-free phthalocyanines is in progress.

As we have previously reported (**6**), the ¹H nmr spectra of monomeric phthalocyanines such as **6** and dimeric phthalocyanines such as 1,3-bis-2'-(9',16',23'-trineopentoxypthalocyaninyl)-2-ethyl-2-methylpropane (**35**) (Fig. 1) and, now, dimers **7a** and **7b** exhibit broad absorptions for internal NH protons in the region of -6.0 ppm when the spectra are run on samples at high concentrations (10^{-1} M) (Table 3). Although these data are consistent in general with those obtained by other workers for simple tetrasubstituted mononuclear phthalocyanines (**24**, **25**), these workers do not record the concentrations of the phthalocyanines on which measurements were made and

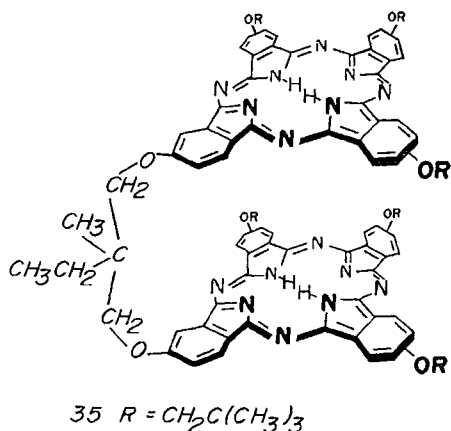


FIG. 1

the reported NH absorbances vary from -2.0 (24) to -9.0 ppm (25), an effect very concentration dependent as shown herein. The effect of concentration on the observation of the NH absorbances of **6** is described in footnote *d* to Table 3 and effectively shows that the absorption changes from -5.5 at $10^{-1} M$ to -3.0 at $10^{-3} M$ and remains constant upon further dilution. Furthermore, at intermediate concentrations ($10^{-2} M$), the observation of two NH absorbances at -4.1 and -3.0 is noted and undoubtedly represents a mixture of free and aggregated phthalocyanines. The effect of temperature on the ^1H nmr of **6** is somewhat complicated by the concomitant effect of solvent on the internal NH absorbances. Thus in toluene- d_8 the NH absorbance (at $10^{-4} M$) at 80°C is -3.0 , at 22°C is -2.60 , and at -80°C is -0.9 ppm. On the other hand, in CD_2Cl_2 the NH absorbance is invariant between -70°C and 22°C and broadens greatly in CDCl_3 at 50°C . Most importantly, however, the higher temperature nmr spectra do not exhibit NH absorbances at significantly lower fields, and hence 10^{-3} – $10^{-4} M$ solutions most likely represent free non-aggregated phthalocyanines even at room temperature. The lack of an upfield shift of the NH absorbances at lower temperatures indicates that conformational mobility is still high enough that aggregation does not appreciably occur at -70 to -80°C . The NH absorbances of the binuclear phthalocyanines (**7b**) and **35** at -70°C in CD_2Cl_2 and $+50^\circ\text{C}$ in CDCl_3 again do not appreciably change their value of ~ -3.1 ppm, which indicates that even at low temperatures in the binuclear phthalocyanines conformational mobility is high on the nmr time scale or that intramolecular cofacial interaction is insignificant. Thus the extent of cofacial conformations of binuclear phthalocyanines **7a, b, 25–27**, and **34–35** cannot be evaluated at present using nmr techniques. The mononuclear phthalocyanine **6** exhibits only a broad absorption peak for the CH_3 groups of the *tert*-butyl substituent in its ^1H nmr spectra at high concentrations ($10^{-1} M$) (Table 3) (**6**) but in dilute solutions (10^{-3} – $10^{-4} M$) **6**, the Zn derivative of **6** (**6Zn**) (**6**), **18** (26), and **19** exhibit 6, 7, 4, and 6 peaks, respectively, corresponding to this *tert*-butyl group. It should be noted that **6**, **6Zn**, **18**, and **19** each exist as a mixture of four possible positional isomers and that these isomers give rise to a total of eight possible environments for the substituent groups. For dilute solutions, up to 7 of these different absorptions are seen for the *tert*-butyl group (Table 3). In fact, for **6Zn** we can clearly see seven single absorptions for the CH_2O group of the mixture of 4 isomers. For dimers **7a, b, 25, 26, 27**, and **34** the ^1H nmr substituent absorbances of the mixtures of isomers are generally broad and not resolvable. As previously

reported (**6**), the ^{13}C nmr of **6** at high concentrations ($10^{-1} M$) exhibited only 1 absorption peak for the CH_3 group of the *tert*-butyl group and, indeed, dimers **7a, 7b, 27**, and **34**, based on the neopentoxy substituent, all exhibited only one or two peaks for this group. On the other hand, the ^{13}C nmr of monomers **18** and **19** exhibited a multiplicity of peaks, again representing the 8 environments in which the four isomers each of **18** and **19** exist (Table 4). Indeed, **18** exhibits two absorptions for the CH_3Si carbon, all eight absorptions for the CH_2Si carbons, and six absorptions for the $\text{CH}_2\text{CH}_2\text{Si}$ carbon (Table 4). The much greater multiplicity of isomers of the dimers and their even greater numbers of environments actually generate rather deceptively simple spectra in which single or small numbers of $(\text{CH}_3)_3\text{Z}$ absorbances are observed (Table 4). Because of this multiplicity of environments, rather poorly resolved, very weak, absorbances are observed in the aromatic region, and the bridging carbons of the dimers and these absorbances are not listed for both ^1H and ^{13}C nmr spectra of compounds in which these absorbances are poorly defined.

All phthalocyanines exhibited parent ions in their mass spectra (**27**) using the FAB system (**14**) and *o*-nitrophenyl octyl ether (ONPOE) as the solvent (**6**). The infrared spectra of all metal-free phthalocyanines exhibited characteristic NH absorptions at 3300 and 1020 cm^{-1} (**28**), which disappeared on formation of their cobalt derivatives.

The mononuclear phthalocyanine bearing the isohexyl substituents (**19**) was clearly less soluble than the tetra-neopentoxyphthalocyanine (**6**) but the tetra-(2-trimethylsilylethyl)phthalocyanine (**18**) was almost as soluble as **6** (Table 2). Thus if one wishes to prepare soluble multinuclear phthalocyanines bearing no oxygen atoms around the periphery of the phthalocyanine nucleus, it would be possible to use isoindoline **16** as a "partner" in condensation reactions, but use of isoindoline **17** gives rather insoluble dimeric phthalocyanines (Table 2). It appears that phthalocyanine dimers containing bridges having oxygen atoms (**7a, b, 35**) are considerably more soluble than all carbon bridge dimers such as **25–27** and **34**. Perhaps, not surprisingly, the more flexible tetramethylene bridged dimer **34** is more soluble than the ethylene bridged dimer **27**. Indeed, only dimers **7a** and **34** in this work exhibit ^{13}C nmr peaks for bridging carbons (Table 4). It was not possible to measure the solubilities of all the phthalocyanines in the same solvent, as **6** and **18** are too soluble in CHCl_3 or *o*-dichlorobenzene (ODCB) to conveniently obtain data while dimers **25–28** and **34** were generally totally insoluble in CH_2Cl_2 . Using the knowledge that the phthalocyanines are generally soluble in solvents in the following order: $\text{CDCl}_3 > \text{CHCl}_3 > \text{ODCB} > \text{CH}_2\text{Cl}_2$, we can generalize from the data shown in Table 2 that the order of solubility of monomeric and dimeric phthalocyanines is **6** (**6**) $>$ **18** $>$ **6Zn** (**6**) $>$ **35** $-$ **7b** $>$ **19** $>$ **20** $>$ **34** $>$ **27** $>$ **25** $>$ **26** $>$ **28**. Thus multinuclear phthalocyanines very soluble in organic solvents are most readily made using the 5-neopentoxyisoindoline **5**, rather than the less accessible 5-alkylisoindolines **16** and **17**, as a partner in mixed condensations with bisisoindolines. In addition, multinuclear phthalocyanines bridged only by carbon atoms are less soluble than their oxygen bridged analogs. This decreased solubility may render their electrocatalytic properties less amenable to study. Further research on the synthesis of binuclear and multinuclear phthalocyanines having a fixed cofacial structure is in progress.

Experimental

Matheson high purity argon was used to maintain inert atmosphere

conditions. Infrared (ir) spectra were recorded on a Pye Unicam SP1000 infrared spectrophotometer using KBr discs for solids or as neat films between NaCl discs. Nuclear magnetic resonance (nmr) spectra for protons were recorded on a Varian LM 360 spectrometer using deuteriochloroform as solvent and tetramethylsilane as the internal standard. The positions of the signals are reported in δ units. (The splittings of the signals are described as singlets (s), doublets (d), triplets (t), quartets (q), or multiplets (m).) A Bruker AM300 nmr spectrometer was used for all ^{13}C nmr spectra and for ^1H nmr spectra of all phthalocyanines unless otherwise stated. The ^1H nmr spectra of 10^{-4} M solutions of phthalocyanines were obtained by averaging 500–1000 scans over the absorption range, while ^{13}C nmr spectra on saturated solutions of phthalocyanine were obtained by averaging 5 000–15 000 scans over the absorption range.

The visible–ultraviolet spectra (uv) were recorded on a Hewlett Packard HP8451A Diode Array spectrophotometer. Mass spectra (ms) were recorded at 70 eV on a VG Micromass 16F mass spectrometer in the EI mode.

The FAB spectra were obtained with a Kratos MS-50 triple analyzer mass spectrometer equipped with a FAB ion source of standard Kratos design and an Ion Tech atom gun. The sample was dissolved in chloroform and a microliter of the resulting solution added to a microliter of *o*-nitrophenyl octyl ether on the probe tip. The spectra of the molecular ions of the binuclear phthalocyanines were obtained by signal averaging up to 256 scans over the appropriate mass range. The number in parentheses after the indicated ion shows the percentage of the base peak represented by that ion. Melting points (mp) were determined using a Kofler hot stage melting point apparatus and are uncorrected. Thin-layer chromatography (tlc) was performed using silica gel G as the adsorbent. Flash chromatography was performed using silica gel of particle size 20–45 μm . All reactions were stirred with a magnetic stirrer. All solvents were freshly distilled before use. Microanalyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ont.

1,2-Bis-(3,4-dicyanophenoxy)-4-tert-butylbenzene (3a) and 1,2-bis-(3,4-dicyanophenoxy)benzene (3b)

A solution of 3.90 g (22.5 mmol) of **1**, 1.66 g (10 mmol) of **2a**, and 7.0 g (50 mmol) of anhydrous potassium carbonate (K_2CO_3) in 25 mL of dry dimethylformamide (DMF) (**6**, **9**) was stirred at room temperature for 36 h. The reaction mixture was diluted with water (150 mL), extracted with ethyl acetate, washed with saturated potassium carbonate, 4 M HCl, water, and saturated sodium chloride, and dried over magnesium sulphate. Evaporation of the solvent gave a brown oil, which on recrystallization from ethyl acetate – petroleum ether gave, in 84% yield, 3.51 g of **3a**, mp 143–143.5°C; ir (cm^{-1}): 2260 (CN), 1595, 1575; ^1H nmr (CDCl_3 , 60 MHz) δ : 7.85–7.05 (m, 9H, ArH), 1.35 (s, 9H, *t*Bu); ms, m/z : 418 (M^+ , 21), 537 (20), 283 (10), 243 (65), 240 (100), 183 (48), 144 (19), 105 (58). *Anal.* calcd. for $\text{C}_{26}\text{H}_{18}\text{N}_4\text{O}_2$: C 74.63, H 4.34, N 13.39; found: C 74.62, H 4.33, N 13.31.

Similarly, a solution of 3.90 g (22.5 mmol) of **1**, 1.1 g (10 mmol) of **2b**, and 7.0 g (50 mmol) of K_2CO_3 in 25 mL of DMF was stirred for 36 h at room temperature. The reaction mixture was extracted with ethyl acetate and worked up as described above to give a crude crystalline product, contaminated by a small quantity of starting material **1**. Column chromatography of this crude mixture on silica gel and elution with 1:5 ethyl acetate – petroleum ether gave **1**. Further elution with 3:2 ethyl acetate – petroleum ether gave, in 78% yield, upon evaporation of the solvent and recrystallization from ethyl acetate – petroleum ether, 2.82 g of colourless needles of **3b**, mp 189–190°C; ir (cm^{-1}): 2260, 1595, 1572; ^1H nmr (CDCl_3 , 60 MHz) δ : 7.80–7.00 (m, 10H, ArH); ms, m/z : 363 (31), 362 (M^+ , 100), 219 (30). *Anal.* calcd. for $\text{C}_{22}\text{H}_{10}\text{N}_4\text{O}_2$: C 72.93, H 2.78, N 15.46; found: C 73.07, H 2.56, N 15.48.

Preparation of isoindolines 4a and 4b

The bis-1,3-diiminoisoindolines **4a** and **4b** were prepared as previously described (**6**, **12**). In a typical example 20 mg of sodium was added to 40 mL of dry methanol under argon to form sodium meth-

oxide. Nitrile **3b** (500 mg, 1.38 mmol) was added and the oil bath heated to 60°C to dissolve the nitrile. Ammonia gas was bubbled into this solution as previously described (**6**) and the methanol evaporated to give crude **4b**, which was used directly in the next step. An ir spectrum of the crude isoindolines must not exhibit any residual nitrile absorption.

1,2-Bis-2'-(9',16',23'-trineopentoxypthalocyaninoxy)-4-tert-butylbenzene (7a) and 1,2-bis-2'-(9',16',23'-trineopentoxypthalocyaninoxy)benzene (7b)

The crude bis-1,3-diiminoisoindoline (**4a**) and 5-neopentoxo-1,3-diiminoisoindoline (**5**) obtained from 200 mg (0.48 mmol) of **3a** and 2.5 g (11.68 mmol) of 4-neopentoxypthalonitrile (**5**, **6**) respectively, were heated at 150–160°C (oil bath) in 20 mL of 2-*N,N*-dimethylaminoethanol for 60 h under an argon atmosphere by methods similar to those previously described (**6**, **12**). The reaction mixture was cooled, poured into water, filtered, and washed repeatedly with water. The crude reaction mixture was dissolved in 200 mL of toluene and stirred at 70°C for 5 h with 100 mL of 1 M KOH. The reaction mixture was cooled; the organic layer was separated from the aqueous layer and washed with water and saturated sodium chloride, and dried over magnesium sulphate. The toluene solution containing the phthalocyanine mixture was preadsorbed onto silica gel for flash chromatography (**13**). Elution with 600 mL of toluene – petroleum ether (5:1) followed by elution with pure toluene gave three initial fractions (200 mL each) followed by fifteen 100-mL fractions and, finally, two 1-L fractions. The early fractions contained pure 2,9,16,23-tetraneopentoxypthalocyanine (**6**), the middle fractions mixtures of **6** and **7a**, and the final fractions mixtures of **7a** and another phthalocyanine thought to be a trinuclear phthalocyanine. The middle fractions containing **6** and **7a** were rechromatographed on fresh silica by flash chromatography using toluene as eluant. Again monomer **6** eluted first, some mixed fractions eluted next, and pure **7a** was finally isolated. All of **7a** was eventually recovered by rechromatography of all mixed fractions. The yield of monomer **6** recovered was 58% (1.45 g). The final fractions containing dimer **7a** and a trimer[†] were also separated by flash chromatography to give, in total, 108 mg (13% yield) of **7a** as a dark, blue, shining solid, mp >300°C; ir (cm^{-1}): 3310 (NH), 1620, 1245, 1100, 1020 (NH); ms m/z : 1707.8 (100), 1706.8 (M^+ , 87). *Anal.* calcd. for $\text{C}_{104}\text{H}_{100}\text{N}_{16}\text{O}_8$: C 73.13, H 6.25, N 13.12; found: C 72.97, H 6.32, N 13.57.

A small fraction of the dimer–trimer mixture was chromatographed on preparative TLC plates using toluene/2-methoxyethanol (200:1) as solvent. The slower moving blue-green fraction was extracted with toluene and finally purified by flash chromatography using toluene/2-methoxyethanol (50:1) as solvent to give a very small quantity of a blue green solid. *Mol. Wt.* (FAB ms) calcd. for $\text{C}_{156}\text{N}_{154}\text{N}_{24}\text{O}_{12}$: 2556.91; found 2556.2 (100), 2555.2 (M^+ , 76).

Similarly, the crude bis-1,3-diiminoisoindoline (**4b**) and **5**, obtained from 500 mg (1.38 mmol) of **3b** and 7.5 g (35.0 mmol) of 4-neopentoxypthalonitrile (**5**, **6**), respectively, gave monomer **6** in the toluene fractions on flash chromatography of the crude product obtained from the reaction mixture. Further elution with toluene/2-methoxyethanol (100:1) and toluene/2-methoxyethanol (200:5) gave mixed monomer–dimer fractions and pure dimer fractions. Rechromatography of the mixed fractions gave a total of 3.15 g of pure monomer **6** in 42% yield and 222 mg (10% yield) of pure dimer **7b** as a dark, blue, shining solid, mp >300°C; ir (cm^{-1}): 3310 (NH), 1625, 1248, 1105, 1020 (NH); ms m/z : 1651.8 (100), 1650.8 (M^+ , 61). *Anal.* calcd. for $\text{C}_{100}\text{H}_{98}\text{N}_{16}\text{O}_8$: C 72.71, H 5.98, N 13.57; found: C 73.24, H 5.98, N 13.19.

1,2-Bis-2'-(9',16',23'-trineopentoxypthalocyaninoxycobalt(II))benzene (7c)

A solution of 100 mg (0.06 mmol) of **7b** and 80 mg of cobalt(II) chloride in 10 mL of toluene/2-methoxyethanol (7:3) was heated at 110°C under argon for 30 h as previously described (**6**). Flash chromatography of the crude product using toluene/2-methoxyethanol (50:1) as eluant gave, in 69% yield, 73 mg of **7c** as a shiny blue solid, mp >300°C; ir (cm^{-1}): 1620, 1250, 1105, 1070, 760; ms m/z : 1765.6

(100), 1764.6 (M^+ , 62). *Anal.* calcd. for $C_{100}H_{94}N_{16}O_8Co_2$: C 68.06, H 5.37, N 12.70, Co 6.68; found: C 68.21, H 5.54, N 12.34, Co 6.44.

4-Aminophthalonitrile (8)

A suspension of 5.19 g (30 mmol) of 4-nitrophthalonitrile (**1**) (**29**) and 0.5–0.6 g of 10% palladium on charcoal in 150 mL of 95% ethanol was placed a 500-mL jar in a Parr hydrogenation apparatus and hydrogenated at 415 kPa according to the procedure of Rasmussen *et al.* (**30**). The crude product (4.2 g, mp 175–178°C) was chromatographed using normal grade silica gel. Elution with benzene–ethyl acetate (3:1) gave 3.6 g (84% yield) of pure white crystals of **8**, mp 179–180°C (lit. (**30**) mp 179–181°C). Compound **8** does deteriorate on standing and is usually directly converted into compound **9** described below.

4-Iodophthalonitrile (9)

A suspension of 4.29 g (30 mmol) of **8** in 60 mL of 2.5 *M* H_2SO_4 was cooled to $-10^\circ C$. A solution of 2.4 g (34 mmol) of sodium nitrite in 5–8 mL of H_2O was added dropwise with stirring, while the temperature of the mixture was kept at -10 to $0^\circ C$. Stirring was continued at $0^\circ C$ for 0.5 h to complete the reaction. The resulting mixture was rapidly filtered by suction filtration and the cool filtrate was added in a small portion to a cool solution of 5.4 g (32 mmol) of potassium iodide in 30 mL of water. The resulting black mixture was allowed to warm to room temperature with stirring. The precipitated black solid was collected by suction filtration, washed with cold water, and dissolved in benzene. The benzene solution was washed with cold water, 5% $NaHCO_3$, cold water, saturated $Na_2S_2O_3$, again with water, dried over $MgSO_4$, filtered, and concentrated to a small volume. Chromatography on 200 g of normal grade silica gel and elution with benzene gave, in 70% yield, 5.3 g of pure **9** as white crystals, mp 142–143°C (lit. (**31**) mp 141–142°C); ir (cm^{-1}): 3020–2960, 2240 (CN), 1580, 940, 850, 845; 1H nmr ($CDCl_3$, 60 MHz) δ : 8.22–8.08 (m, 2H, ArH-3,6), 7.61–7.55 (m, 1H, ArH-5); ms m/z : 254 (M^+ , 87), 127 (100), 100 (38).

4-(2-Trimethylsilylethynyl)phthalonitrile (12) and 4-(3,3-dimethyl-1-butynyl)phthalonitrile (13)

To a solution of 5.08 g (20 mmol) of **9** in 80 mL of dry, freshly distilled diethylamine was added 2.1 g (22 mmol) of triethylsilylacetylene (**10**), 38 mg (0.2 mmol) of copper(I) iodide, and 140 mg (0.2 mmol) of bis(triphenylphosphine)palladium dichloride under an argon atmosphere, using the procedure of Takahashi *et al.* (**16**). The reaction mixture was stirred at room temperature for 3 h, during which time a precipitate of diethylamine hydroiodide appears. The mixture was filtered to separate the precipitated salt and the filtrate was concentrated on the rotary evaporator. The residue was extracted into benzene and purified by column chromatography on neutral alumina, activity II–III, using benzene as the eluting solvent. Evaporation of the solvent gave an oil which, on distillation in a Kugelrohr apparatus at 110–120°C/0.01 Torr (1 Torr = 133.3 Pa), gave 3.4 g (75% yield) of a white solid (**12**), mp 74–75°C; ir (cm^{-1}): 3100, 2240 (CN), 1600, 1498, 1440, 1345, 1265, 1250, 860, 840; 1H nmr (CCl_4 , 60 MHz) δ : 7.65–7.52 (m, 3H, ArH), 0.05 (s, 9H, $(CH_3)_3Si$); ms m/z : 224 (M^+ , 17), 209 (100), 179 (14), 73 (70), 59 (27), 43 (23). *Anal.* calcd. for $C_{13}H_{12}N_2Si$: C 69.59, H 5.39, N 12.49; found: C 69.51, H 5.53, N 12.19. Product **12** rapidly decomposed in the presence of water.

Similarly, a mixture of 2.54 g (10 mmol) of **9**, 0.82 g (10 mmol) of *tert*-butylacetylene (**11**), 20 mg (0.1 mmol) of copper(I) iodide, and 140 mg (0.2 mmol) of bis(triphenylphosphine)palladium dichloride in 50 mL of dry, freshly distilled diethylamine was stirred overnight under an argon atmosphere. Analysis by thin-layer chromatography (tlc), using ether–hexane 1:4 as eluant, showed the presence of unreacted **9**. An additional 0.16 g of **11** was added and stirring was continued for a further 12 h. A final addition of 0.16 g of **11** was added and, after stirring for a total of 72 h, the reaction was still not completed. The reaction mixture was worked up as described above. Flash chromatography of the crude product using 1:19 ether–hexane as eluant gave an oil, which on distillation in a Kugelrohr apparatus at 130–135°C/0.01 Torr yielded 1.6 g (75% yield) of pure **13**, mp

60–61°C; ir (cm^{-1}): 3100, 3000, 2250 (CN), 2235, 1600, 1490, 1370, 1320, 1275, 910, 880; 1H nmr ($CDCl_3$, 300 MHz) δ : 7.77–7.67 (m, 3H, ArH), 1.32 (s, 9H, $(CH_3)_3C$); ms m/z : 208 (M^+ , 20), 193 (100), 178 (13), 165 (18). *Anal.* calcd. for $C_{14}H_{12}N_2$: C 80.73, H 5.81, N 13.45; found: C 80.70, H 5.90, N 13.21.

4-(2-Trimethylsilylethyl)phthalonitrile (14), 4-ethylphthalonitrile (30), and 4-(3,3-dimethylbutyl)phthalonitrile (15)

A solution of 2.8 g (12.5 mmol) of **12** in 50 mL of dry ethyl acetate was hydrogenated over 10% palladium on charcoal at 275 kPa for 1 h. The catalyst was filtered and the filtrate evaporated to dryness. Column chromatography of the product on 150 g of normal grade silica gel using ethyl acetate–hexane (1:4) as eluant gave, upon evaporation of the solvent, 2.5 g (88% yield) of colourless needles. Distillation of the solid product in a Kugelrohr apparatus at 140–145°C/0.1 Torr gave pure **14**, mp 63–64°C; ir (cm^{-1}): 3090, 2970, 2240 (CN), 1605, 1498, 1345, 1265, 1250, 860, 840, 700; 1H nmr ($CDCl_3$, 300 MHz) δ : 7.60–7.45 (m, 3H, ArH), 2.71 (m, 2H, CH_2ArH), 0.84 (m, 2H, CH_2Si), 0.01 (s, 9H, $(CH_3)_3Si$); ms m/z : 228 (M^+ , 41), 213 (35), 73 (100), 59 (68), 43 (17). *Anal.* calcd. for $C_{13}H_{16}N_2Si$: C 68.36, H 7.06, N 12.26; found: C 68.11, H 7.18, N 12.29.

Further elution of the silica gel gave 0.1 g of 4-ethylphthalonitrile (**30**) as a white solid, mp 42–43°C; ir (cm^{-1}): 3000–2900, 2245 (CN), 1600, 1500, 1240, 1070, 870, 850; 1H nmr ($CDCl_3$, 60 MHz) δ : 7.8–7.4 (m, 3H, ArH), 2.8 (q, $J = 8$ Hz, 2H, CH_2), 0.84 (t, $J = 8$ Hz, 3H, CH_3); ms m/z : 156 (M^+ , 50), 141 (100), 114 (40). *Anal.* calcd. for $C_{10}H_8N_2$: C 76.90, H 5.16, N 17.94; found: C 77.23, H 5.33, N 17.99.

Similarly, hydrogenation of 3.6 g (17 mmol) of **13** in 100 mL of dry ethanol for 1 h as described above yielded a crude oil. Flash chromatography of this oil using ether–hexane (1:9) as eluant and distillation of product using a Kugelrohr apparatus gave 3.3 g (92% yield) of **15** as a colourless oil, bp 130–138°C/0.01 Torr; ir (neat, cm^{-1}): 2980, 2250 (CN), 1610, 1500, 1380, 1250, 850; 1H nmr ($CDCl_3$, 300 MHz) δ : 7.80–7.78 (m, 1H, ArH), 7.65–7.58 (m, 2H, ArH), 2.74–2.68 (m, 2H, CH_2Ar), 1.54–1.48 (m, 2H, CH_2C), 1.33 (s, 9H, $(CH_3)_3C$). *Anal.* calcd. for $C_{14}H_{16}N_2$: C 79.20, H 7.59, N 13.20; found: C 79.05, H 7.49, N 13.05.

Preparation of 5-(2-trimethylsilylethyl)-1,3-diiminoisoindoline (16) and 5-(3,3-dimethylbutyl)-1,3-diiminoisoindoline (17)

All diiminoisoindolines were prepared as previously described (**5**, **6**, **11**, **12**). In a typical example 115 mg (0.50 mmol) of **14** was added to a solution of 15 mg of sodium in 10 mL of dry methanol. The mixture was stirred at room temperature for 1 h and for 4 h under reflux conditions, during which ammonia gas was bubbled into the solution. Evaporation of the solvent gave crude **16**, which was used directly in condensation reactions without further purification. Compounds **16** and **17** did not exhibit nitrile absorptions in their ir spectra.

Preparation of 2,9,16,23-tetra-(2-trimethylsilylethyl)phthalocyanine (18) and 2,9,16,23-tetra-(3,3-dimethylbutyl)phthalocyanine (19)

The crude diiminoisoindoline **16**, obtained from 115 mg (0.50 mmol) of **14** in 2 mL of 2-*N,N*-dimethylaminoethanol, underwent self-condensation as previously described (**5**, **6**, **11**, **12**) to give 60 mg of a crude reaction product. Flash chromatography of this product using toluene as eluant gave, upon evaporation of the solvent, 33 mg (28% yield) of **18** as a dark blue, shining solid; ir (cm^{-1}): 3310 (NH), 1620, 1255, 1100, 1015 (NH), 870, 840, 760; ms m/z : 915 (M^+ , 100), 841 (28). *Anal.* calcd. for $C_{52}H_{66}N_8Si_4$: C 68.22, H 7.27, N 12.24; found: C 68.31, H 6.99, N 12.24.

Similarly, the crude diiminoisoindoline **17**, obtained from 118 mg (0.56 mmol) of **13** in 2 mL of 2-*N,N*-dimethylaminoethanol, underwent self-condensation as previously described (**5**, **6**, **11**, **12**) to give 90 mg of a crude reaction product. Flash chromatography of this product using toluene as eluant gave, upon evaporation of the solvent, 48 mg (40% yield) of **19** as a dark blue, shining solid; ir (cm^{-1}): 3320 (NH), 1625, 1105, 1020 (NH), 760; ms m/z : 850 (M^+ , 100), 791 (35), 424 (47). *Anal.* calcd. for $C_{50}H_{66}N_8$: C 79.02, H 7.82, N 13.16; found: C 78.71, H 7.76, N 13.09.

2,9,16,23-Tetra-(3,3-dimethylbutyl)phthalocyaninatocobalt(II) (20)

To a solution of 153 mg (0.18 mmol) of **19** in 15 mL of toluene and 5 mL of 2-methoxyethanol was added 91 mg (0.70 mmol) of anhydrous cobalt(II) chloride as previously described (6). The solution was stirred at 115°C (oil bath) under an argon atmosphere for 19 h. The crude reaction mixture was cooled to room temperature and the solvent evaporated. Flash chromatography of the residue using toluene as the eluting solvent gave, in 48% yield, 78 mg of **20** as a dark blue, shining solid; ν (cm⁻¹): 1625, 1105, 760; m/z : 908 (M⁺, 75), 850 (21). *Anal.* calcd. for C₅₆H₆₄N₄Co: C 74.07, H 7.10, N 12.34, Co 6.49; found: C 74.50, H 7.64, N 11.58, Co 6.50.

1,2-Bis-(3,4-dicyanophenyl)ethyne (22) and 1,2-bis-(3,4-dicyanophenyl)ethane (23)

By the procedure described above for the preparation of **12** and **13**, 5.1 g (20 mmol) of **9**, 150 mL of dry, freshly distilled diethylamine, 38 mg (0.2 mmol) of copper(I) iodide, and 70 mg (0.1 mmol) of bis(triphenylphosphine)palladium dichloride was placed into a 250-mL two-necked flask, equipped with a magnetic stirrer, a condenser, and a gas inlet tube. The flask was flushed with argon and a moderate stream of dry acetylene was passed through the solution for 3 h at room temperature. The pale pink precipitate that was formed was collected by filtration from the brown solution. The crude product was washed with water, methanol, and ether, and air dried to give, in 90% yield, 2.5 g of **22**, mp 286–288°C. This product is sufficiently pure that it can be used directly without further purification. Two recrystallizations of a small sample of **22** from acetonitrile gave colourless crystals of pure **22**, mp 296–297°C; ν (cm⁻¹): 3090, 2240 (CN), 1600, 1500, 1260, 920, 865; m/z : 278 (M⁺, 100), 251 (14), 224 (8), 149 (35), 139 (11), 85 (38), 57 (97), 43 (73). *Anal.* calcd. for C₁₈H₆N₄: C 77.69, H 2.17, N 20.13; found: C 77.97, H 1.96, N 20.01. Compound **22** is very insoluble in common organic solvents and is only slightly soluble in boiling acetonitrile (100 mg in 50 mL). The ¹H and ¹³C nmr of **22** was not determined, as a suitable solvent was not found in which **22** was sufficiently soluble.

A suspension of 0.6 g (2.1 mmol) of **22** in 300 mL of acetonitrile, containing 100 mg of 10% palladium on charcoal, was hydrogenated at 415 kPa in a Parr hydrogenation bottle for 4 h at room temperature. The clear solution was filtered from the catalyst and concentrated. The compound was purified by flash chromatography using hot acetonitrile as eluant to give 0.5 g (83% yield) of **23** as white needles, mp 257–258°C; ν (cm⁻¹): 3100, 2980, 2240 (CN), 1600, 1490, 1390, 1240, 925, 860; ¹H nmr (CD₃CN, 400 MHz) δ : 7.81 (d, *J* = 8 Hz, 2H, ArH-5), 7.76 (s, 2H, ArH-2), 7.58 (d, *J* = 8 Hz, 2H, ArH-6), 3.05 (s, 4H, CH₂); m/z : 282 (M⁺, 31), 141 (100), 114 (49), 57 (73), 39 (11). *Anal.* calcd. for C₁₈H₁₀N₄: C 76.58, H 3.57, N 19.84; found: C 76.76, H 3.47, N 19.94.

Preparation of the bis-1,3-diiminoisoindoline (24)

Compound **24** was prepared as previously described (6) for the preparation of 1,3-diiminoisoindolines derived from bisphthalonitriles only slightly soluble in methanol.

1,2-Bis-2'-(9',16',23'-tri-(2-trimethylsilylethyl)phthalocyaninyl)ethane (25)

The two crude diiminoisoindolines **16** and **24**, obtained from 4.80 g (21.1 mmol) of **14** and 203 mg (0.72 mmol) of **23**, respectively, in 30 mL of 2-*N,N*-dimethylaminoethanol, underwent a mixed condensation as previously described (5,6) to give 5 g of a crude reaction product. Flash chromatography on silica gel of this product on a 5-cm diameter column using toluene–hexane (1:1) as eluant gave 1.63 g of the monomeric **18** in 34% yield. Further elution with toluene gave a fraction consisting largely of dimer. This dimer fraction was purified further by flash chromatography on a 3-cm diameter column. Elution with toluene–hexane (1:1) removed all traces of monomer, as analyzed by tlc using toluene as eluant. Further elution with toluene gave a blue solid containing a trace of impurities, detected by tlc analysis and visualization with uv light. The blue solid was freed of these impurities by washing with methanol to give, in 7% yield, 83 mg of the binuclear phthalocyanine **25** as a dark blue, shining solid; ν (cm⁻¹): 3320 (NH), 1620, 1260, 1105, 1020 (NH), 870, 840, 760; m/z : 1659 (48), 1658 (63), 1657 (100), 1656 (91), 1655 (M⁺, 65). *Anal.* calcd. for C₉₆H₁₁₀N₁₆Si₆: C 69.61, H 6.69, N 13.53; found: C 69.65, H 6.80, N 13.16.

Anal. calcd. for C₉₆H₁₁₀N₁₆Si₆: C 69.61, H 6.69, N 13.53; found: C 69.65, H 6.80, N 13.16.

1,2-Bis-2'-(9',16',23'-tri-(3,3-dimethylbutyl)phthalocyaninyl)ethane (26)

The two crude diiminoisoindolines **17** and **24**, obtained from 4.46 g (21.0 mmol) of **15** and 203 mg (0.72 mmol) of **23**, respectively, in 30 mL of 2-*N,N*-dimethylaminoethanol, underwent a mixed condensation as described for **7a**, **7b**, and **25** above and previously (5, 6) to give 5 g of a crude reaction product. Flash chromatography of this product on silica gel (5-cm diameter column) using toluene–hexane (1:1) and pure toluene gave 2.07 g of the monomeric phthalocyanine **19** containing traces of dimer, as analyzed by tlc using toluene as eluant. Further elution with 2-methoxyethanol/toluene (1:100) gave a fraction consisting largely of dimer containing traces of monomer. Finally, elution with 2-methoxyethanol/toluene (1:4) gave a green fraction consisting largely of trimer and impurities. The solid monomer fraction was placed in the thimble of a Soxhlet extractor and extracted with refluxing hexanes to give 0.52 g of pure monomer **19**. Using the Soxhlet extractor and refluxing toluene as solvent, a further 0.71 g of **19** was isolated from the extracting solvent on evaporation, leaving 0.84 g of insoluble monomer containing traces of dimer in the thimble. It is possible that some of the positional isomers of **19** are more soluble than others and that the above selective extraction has effected a partial separation of these isomers. The dimer fraction was purified by vacuum liquid chromatography (vlc) (32) using toluene–hexanes (1:1) as the eluting solvent followed by increasing amounts of 2-methoxyethanol/toluene (1:100 to 5:100). The vlc removed most of the monomer (but not all) and a final separation was achieved by flash chromatography (13) using the same eluting solvents as above to give, in 8% yield, 90 mg of the pure binuclear phthalocyanine **26** as a dark blue, shining solid; ν (cm⁻¹): 3320 (NH), 1625, 1105, 1015 (NH), 760; m/z : 1561 (84), 1560 (100), 1559 (M⁺, 84). *Anal.* calcd. for C₁₀₂H₁₁₀N₁₆: C 78.53, H 7.11, N 14.36; found: C 79.36, H 7.62, N 13.49.

1,2-Bis-2'-(9',16',23'-trineopentoxypthalocyaninyl)ethane (27)

The two crude diiminoisoindolines **5** and **24**, obtained from 6.0 g (28 mmol) of 4-neopentoxypthalonitrile (**5**, **6**) and 284 mg (1.0 mmol) of **23**, were heated to 150°C (oil bath) in 30 mL of 2-*N,N*-dimethylaminoethanol for 60 h under argon as previously described (5, 6). The crude product was purified by flash chromatography using a 5-cm diameter column packed with silica gel 12 cm high. The crude product was preabsorbed on silica and eluted with toluene to give 2.67 g of the monomeric **6** in 44% yield. Further elution with 2-methoxyethanol/toluene (1:100) gave a fraction consisting largely of dimer containing traces of monomer and some green material. Finally, elution with 2-methoxyethanol/toluene (1:4) gave a green fraction consisting largely of trimer and impurities. The dimer fraction was further purified by flash chromatography (3-cm diameter column). Elution with toluene removed all traces of monomer. Further elution with 2-methoxyethanol/toluene (5:200) gave a dark blue product. This product was washed with acetone to remove traces of fluorescent and light green impurities, detectable by tlc using toluene/2-methoxyethanol (200:5) as eluant, to give in 10% yield 159 mg of **27** as a dark blue, shining solid; ν (cm⁻¹): 3310 (NH), 1620, 1245, 1100, 1020 (NH), 755; m/z : 1574.8 (51), 1572.8 (90), 1571.8 (100), 1570.8 (M⁺, 60). *Anal.* calcd. for C₉₆H₉₈N₁₆O₆: C 73.35, H 6.28, N 14.26; found: C 73.08, H 6.34, N 14.19.

The "trimer" fraction was further purified by flash chromatography (3-cm diameter column). Elution with 2-methoxyethanol/toluene (3:200) removed all traces of dimer. Further elution with 2-methoxyethanol/toluene 1:20 gave 280 mg of a dark, blue, shining solid in 25% yield. This product was not characterized.

1,2-Bis-2'-(9',16',23'-trineopentoxypthalocyaninyl cobalt(II))ethane (28)

A mixture of 44 mg (0.028 mmol) of metal-free dimer **27** and

21 mg (0.16 mmol) of anhydrous cobalt(II) chloride in 13 mL of a 1:4 mixture of 2-methoxyethanol/toluene was heated at 120°C for 20 h under an argon atmosphere. Flash chromatography of the crude reaction mixture on a 3-cm diameter column of silica gel and elution with 2-methoxyethanol/toluene (1:20 and then 1:8) gave, in 55% yield, 26 mg of **28** as a dark blue, shining solid; ν (cm⁻¹): 1620, 1245, 1100, 760; m/z : 1687.6 (49), 1686.6 (80), 1685.6 (100), 1684.6 (M⁺, 76), 1630.6 (38), 1629.6 (57), 1628.6 (72), 1627.6 (51). *Anal.* calcd. for C₉H₉N₁₆O₆Co₂: C 68.40, H 5.62, N 13.29, Co 6.99; found: C 68.06, H 5.75, N 12.95, Co 7.19.

4-Ethynylphthalonitrile (**29**)

Preliminary experiments conducted on the hydrolysis of **12** to **29** showed that hydrolysis was slow in pyridine alone, pyridine and methanol, or pyridine and copper(II) acetate, and that all three components are necessary for rapid hydrolysis. These conditions are identical with those necessary for the coupling of terminal alkynes by the Eglinton procedure (20) except that hydrolysis occurs at room temperature. A solution of 0.09 g (0.4 mmol) of **12**, 1.6 g of copper(II) acetate monohydrate, 0.8 mL of methanol, and 14 mL of pyridine was stirred for 1 h at room temperature. The reaction mixture was filtered and washed with pyridine and methanol. The filtrate was evaporated to dryness *in vacuo* and extracted with methylene chloride. The extract was washed with water, dilute hydrochloric acid, and water, and dried over MgSO₄. Evaporation of the solvent gave a product which was purified by flash chromatography, using ethyl acetate-hexane (1:4) as eluant. Evaporation of the eluant gave, in 82% yield, 50 mg of pure **29** as white crystals, mp 88–90°C; ν (Nujol, cm⁻¹): 3280 (≡C—H), 2250, 2135, 1600, 930, 850; ¹H nmr (CDCl₃, 60 MHz) δ : 8.0–7.8 (m, 3H, ArH), 3.45 (s, 1H, ≡C—H); m/z : 152 (M⁺, 100), 125 (46), 99 (28), 74 (26), 50 (37). *Anal.* calcd. for C₁₀H₄N₂: C 78.94, H 2.68, N 18.41; found: C 78.28, H 3.00, N 18.60.

Further elution of the silica gel gave 10 mg of **31** described below.

1,4-Bis-(3,4-dicyanophenyl)-1,3-butadiyne (**31**)

Using the Eglinton terminal alkyne coupling procedure (20) and recognizing that **12** gives **29** under the conditions of this reaction, 0.45 g (2.0 mmol) of **12** was mixed with 8.0 g of copper(II) acetate monohydrate in 70 mL of dry pyridine and 4 mL of dry methanol. The mixture was heated at 50–55°C for 0.75 h with stirring under argon. The reaction mixture was cooled to room temperature, filtered, and washed with pyridine and methanol. The filtrate was worked up as described for **29** above to give, in 76% yield, 0.23 g of a crude product, mp 299–302°C. Further purification by flash chromatography on silica gel using CH₂Cl₂ as eluant gave, upon evaporation of the solvent, in 70% total yield 0.21 g of pure white crystals of **31**, mp 303–304°C; ν (cm⁻¹): 3100, 2250 (CN), 2180 (C≡C), 1600, 1300, 1240, 925, 860; ¹H nmr (CD₂Cl₂, 60 MHz) δ : 7.9–7.7 (m, 6H, ArH); m/z : 302 (M⁺, 100), 275 (7), 248 (5), 224 (8), 200 (8), 151 (8), 124 (4), 98 (4), 74 (4). *Anal.* calcd. for C₂₀H₆N₄: C 79.46, H 1.99, N 18.54; found: C 79.39, H 1.81, N 18.48.

1,4-Bis-(3,4-dicyanophenyl)butane (**32**)

A solution of 0.15 g (0.5 mmol) of **31** in 100 mL of dry tetrahydrofuran (THF) and 50 mg of 10% palladium on charcoal was hydrogenated at 275 kPa in a Parr hydrogenator for 1 h at room temperature. The catalyst was filtered over Celite and washed with THF. The filtrate was evaporated to give fine colourless crystals in quantitative yield. Further purification by flash chromatography on silica gel using CH₂Cl₂-ether (1:10) gave 0.13 g in 84% yield of pure **32**, mp 168–169°C; ν (cm⁻¹): 3100, 2950, 2240 (CN), 1600, 1500, 1250, 860, 850; ¹H nmr (CD₂Cl₂, 400 MHz) δ : 7.73 (d, *J* = 8 Hz, 2H, ArH-5), 7.62 (s, 2H, ArH-2), 7.53 (d, *J* = 8 Hz, ArH-6), 2.77 (t, *J* = 8 Hz, 4H, ArCH₂), 1.67 (m, 4H, CH₂); m/z : 310 (M⁺, 39), 169 (26), 155 (58), 141 (100), 114 (41), 39 (13). *Anal.* calcd. for C₂₀H₁₄N₄: C 77.39, H 4.55, N 18.05; found: C 77.62, H 4.35, N 17.97.

Preparation of the bis-1,3-diiminoisoindoline (**33**)

Compound **33** was prepared as previously described (6) for the

preparation of 1,3-diiminoisoindolines derived from bisphthalonitriles only slightly soluble in methanol.

1,4-Bis-2'-(9',16',23'-trineopentoxypthalocyaninyl)butane (**34**)

The two crude diiminoisoindolines **5** and **33**, obtained from 6.0 g (28 mmol) of 4-neopentoxypthalonitrile (**5**, **6**) and 310 mg (1.0 mmol) of **32**, respectively, were heated to 150°C (oil bath) in 30 mL of *N,N*-dimethylaminoethanol for 60 h under argon as described for the preparation of **27**. Using a work-up identical to that for **27**, purification by flash chromatography as before gave 1.64 g of monomer **6** in 27% yield and, in 1.4% yield, 23 mg of dimer **34** as a dark blue, shining solid; ν (cm⁻¹): 3320 (NH), 1620, 1250, 1105, 1020 (NH), 760; m/z : 1561.8 (25), 1560.8 (85), 1599.8 (100), 1598.8 (M⁺, 64). *Anal.* calcd. for C₉₈H₁₀₂N₁₆O₆: C 73.57, H 6.42, N 14.01; found: C 72.91, H 6.62, N 13.65.

Acknowledgements

We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of this research. This work was also partially funded by the Office of Naval Research (Washington) and by the Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrumentation Facility (Grant No. CHE 8211164).

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