Synthesis, Characterization and Electrical Properties of Phthalocyanines substituted with 17-membered Trioxadiaza Macrocycles

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New phthalocyanines (M = Cu, Zn, Ni, Co or 2H) substituted with four 17-membered trioxadiaza macrocycles have been prepared. Detosylation of aza groups with concentrated sulfuric acid simultaneously leads to sulfonated groups on the aromatic rings of the macrocyclic substituents. While the *N*-tosylated derivatives are soluble in organic solvents, the detosylated ones are extremely soluble in water. The electrical conductivities of the phthalocyanines measured as gold sandwiches are about 10^{-12} S m^{-1} *in vacuo* and show some increase in the presence of dry air.

Apart from their intrinsic use as dyes and pigments, phthalocyanines show a number of special properties which account for the great research interest related to exciting future prospects.[1] Among these we may cite electrochromism,[2] discotic mesophase formation,[3] enhanced electrical conductivity[4] and photosensitive materials for photodynamic therapy.[5] The exceptionally high thermal and chemical stability of the phthalocyanine core results in a versatile chemical system. An infinite number of variations is possible by varying the central metal ion or peripheral substituents.

Our primary goal has been to add macrocyclic substituents on the periphery. We have started with oxa macrocycles (*i.e.* crown ethers) which give extremely soluble products having also alkali-metal binding properties.[6–10] Mesophase and ion-channel formation are prospects with these substituents.[11] The effect of a monoaza crown ether on the periphery is the same with the additional advantage of solubility in water over a wide pH range by quaternization of the aza function.[12,13] Fourteen- or 15-membered tetraaza macrocyclic substituents allow the co-ordination of different transition-metal ions and hence heteropentanuclear products.[14,15]

In an endeavour to extend the range of available macrocycle-substituted phthalocyanines, we have designed a new phthalocyanine with diazatrioxa macrocyclic substituents. While the combination of these two donor groups is expected to result in the co-ordination of both alkali- and transition-metal ions, though less stable than either crown ether alkali-metal complexes or tetraaza macrocycle transition-metal complexes, these new heteronuclear compounds are expected to carry loosely co-ordinated metal ions on the macrocyclic substituents. We herein report studies on phthalocyanines substituted with four 17-membered trioxadiaza macrocycles.

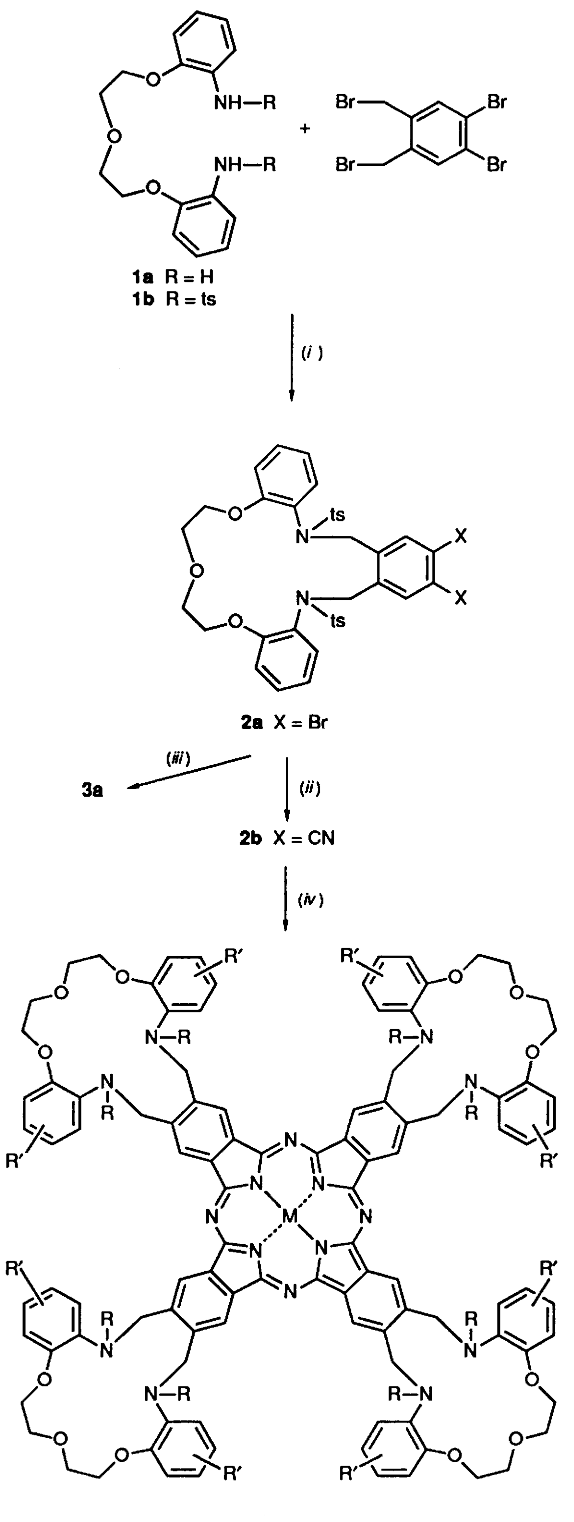
Results and Discussion

As in the case of most other substituted phthalocyanines a rational method for this type of compounds is to start with the dibromo or dicyano derivative of the corresponding macrocyclic compound. For this purpose the tribenzotrioxadiazacycloheptadecine **2a** was obtained by the reaction of 1,2-dibromo-4,5-bis(bromomethyl)benzene with 1,1′-oxybis(ethyleneoxy)-bis(2-toluene-*p*-sulfonylaminobenzene) **1b** in ethanol in the presence of anhydrous potassium carbonate[14,15] (Scheme 1). The relatively high yield of this cyclization reaction between two bifunctional reactants is a clear indication of the template effect of potassium ion.[16] While tosyl groups are also effective in the cyclization, they are used as protective groups for the aza functions in the cyclotetramerization to form the phthalocyanine.

Compound **2a** was converted into the phthalocyaninatocopper(II) derivative **3a** directly by reaction with CuCN in tetramethylurea (tmu). This unique reaction forms an advantageous basis for the synthesis of compound **3a** whereas the other metallophthalocyanines require phthalic acid derivatives as starting materials. For the latter the dicyano derivative **2b** was isolated through the Rosenmund–von Braun reaction which might be considered to be an intermediate step in the phthalocyanine formation. The reaction of **2a** in high-boiling anhydrous solvents (*e.g.* quinoline or ethylene glycol) with the appropriate metal salt gave the monomeric phthalocyanines **3**–**7** (M = Cu^{II}, Ni^{II}, Zn^{II}, Co^{II} or 2 H). The yields were rather low and depended upon the metal ion. A common feature of the *N*-tosyl derivatives is their solubility in various organic solvents. Complexation experiments for trioxadiaza carried out both with transition-metal and alkali-metal ions indicated no binding in the case of *N*-tosylated phthalocyanines **3**–**7**.

Although other detosylation methods under milder conditions had been tried, complete detosylation was accomplished only in concentrated sulfuric acid at elevated temperature (125–130 °C). However, this leads to products with sulfonyl groups on the aromatic rings of the macrocycle. Consequently, the product is a mixture of regioisomers. The elemental analysis results indicate the presence of eight SO_3H groups for each phthalocyanine along with four H_2SO_4 bound to the aza functions which can easily be removed by neutralization (Table 1). Addition of these polar groups gave phthalocyanines which are extremely soluble in water. Conversion of the eight SO_3H groups to the same number of SO_3Na groups was carried out simply by neutralization with NaOH and the products were also extremely soluble in water.

Since sulfophthalocyanines are preferred for some applications (*e.g.* photosensitizers in the photodynamic therapy of



	M	R	R'
3a	Cu	ts	H
3b	Cu	H	SO_3H
3c	Cu	H	SO_3Na
4	Ni	ts	H
5	Zn	ts	H
6a	Co	ts	H
6b	Co	H	SO_3H
6c	Co	H	SO_3Na
7	2H	ts	H

Scheme 1 ts = Tosyl (p-$MeC_6H_4SO_2$). (*i*) EtOH, K_2CO_3; (*ii*) CuCN, $HCONMe_2$; (*iii*) CuCN, tmu, 185–190 °C; (*iv*) metal salt, quinoline, ethylene glycol or 1-chloronaphthalene

Table 1 Analytical* and thermal data for the starting materials and the phthalocyanines

		Analysis (%)			Decomposition temperature/°C	
Compound	Colour	C	H	N	Initial	Main
1b	White	60.00 (60.40)	5.35 (5.40)	5.30 (4.70)		
2a	White	53.25 (53.30)	4.25 (4.25)	3.20 (3.30)	325	365
2b	White	64.55 (64.15)	5.00 (4.85)	7.30 (7.50)	350	420
3a	Green	62.30 (62.80)	4.70 (4.75)	7.80 (7.30)	350	430
3b·$4H_2SO_4$	Blue	43.85 (43.60)	4.15 (4.00)	8.05 (7.80)	275	400
3c	Blue	47.20 (47.15)	4.00 (3.65)	8.75 (8.45)	125	325
4	Blue	63.00 (62.90)	4.70 (4.75)	7.50 (7.35)	385	435
5	Green	62.60 (62.80)	4.85 (4.75)	7.60 (7.35)	325	435
6a	Dark blue	62.45 (62.90)	4.90 (4.75)	6.90 (7.35)	350	420
6b·$4H_2SO_4$	Dark blue	43.15 (43.65)	3.65 (3.40)	8.10 (7.85)	215	425
6c	Dark blue	47.55 (47.20)	4.00 (3.65)	8.25 (8.45)	275	625
7	Green	64.35 (64.10)	4.30 (4.10)	7.90 (7.50)	325	435

* Required values are given in parentheses.

tumours[17]) this substitution can be tolerated. Two disadvantages of sulfo groups are the inapplicability of alkali-metal extraction tests to determine the alkali-metal binding property[7,18] and the difficulty in isolating weakly bound transition-metal complexes of N_2O_3 macrocycles.[19] Characterization of the products involved a combination of methods including elemental and thermal analysis (Table 1), ^1H and ^{13}C NMR (Tables 2 and 3), UV/VIS (Table 4) and IR spectroscopies.

A diagnostic feature of the phthalocyanine formation from the dicyano derivative **2b** is the disappearance of the sharp C≡N vibration at 2220 cm^{-1} of the reactant. The rest of the spectrum is closely similar to that of **2b** including the characteristic vibrations of tosyl and ether groups. Detosylation is verified by changes in the SO_2 stretches around 1160 and 1340 cm^{-1} for the tosylated compounds and 1220 and 1040 cm^{-1} for the sulfo-products. The band around 3420 cm^{-1} for **7** can be attributed to the N–H stretching frequency of the inner core of the metal-free phthalocyanine.

A common feature of the ^1H NMR spectra of metal-free and zinc(II) phthalocyanines is the broad absorptions probably caused by the aggregation of phthalocyanines which is frequently encountered at the concentrations used for NMR measurements.[1,7] Also the NH protons of the metal-free phthalocyanine **7** could not be observed due to this phenomena. Because of the distinct ring current of the 18π-electron system of the inner phthalocyanine core, the protons are characteristically shifted to low or high field[20] (Table 2). However the shifts are rather small for the protons sufficiently far away from the ring current (*e.g.* CH_2O). Proton-decoupled ^{13}C NMR measurements have also been carried out, but complete assignment of the signals is not possible (Table 3). The bands due to the phthalocyanine moiety are comparable with reported values for soluble crown ether-substituted phthalocyanines.[8]

The phthalocyanines **3**–**7** show typical electronic spectra with two strong absorption regions, one of them in the UV region at about 300–350 nm (B band) and the other in the visible portion at 600–700 nm (Q band) (Table 4). In extremely dilute solutions (*ca.* 10^{-6} mol dm^{-3}) the molecules are present as monomers in

Table 2 Proton NMR spectral data for the reactants and the phthalocyanines in $CDCl_3$

Compound	tosyl-CH_3	OCH_2	NCH_2	Aromatic protons
1a	2.24 (6 H, s)	3.82 (4 H, t), 4.04 (4 H, t)	—	6.81–7.64 (16 H, m)
2a^a	2.41 (6 H, s)	3.10–4.53 (8 H, m)	4.85 (4 H, s)	6.72–7.73 (18 H, m)
2b^a	2.44 (6 H, s)	3.34 (4 H, t), 3.92 (4 H, t)	4.73 (4 H, s)	6.73–7.88 (18 H, m)
5^a	2.38 (24 H, s)	3.37 (16 H, t), 4.09 (16 H, t)	5.08 (16 H, s)	6.85–7.60 (72 H, m)
7^{a,b}	2.51 (24 H, s)	3.32 (16 H, t), 3.70 (16 H, s)	4.70 (16 H, s)	7.24–7.91 (72 H, m)

^{a} Broad resonances. ^{b} In $(CD_3)_2SO$.

Table 3 Carbon-13 NMR spectral data for the ligand and its phthalocyanines in $CDCl_3$

Compound	CH_3	NCH_2	OCH_2	Aromatic and nitrile carbons
2a*	20.92	46.42	65.75, 66.74	112.57, 120.33, 122.75, 124.75, 127.18, 129.32, 130.17, 133.73, 136.94, 142.30, 154.77
2b	21.51	48.75	66.20, 68.50	111.98, 114.23, 115.36, 121.23, 127.78, 129.15, 130.25, 133.26, 142.06, 143.50, 154.86
5	21.23	30.21	67.84, 71.96	108.60, 111.80, 121.03, 127.85, 129.05, 136.78, 138.76, 140.14, 142.84, 155.57, 163.24
7	21.02	33.16	61.83, 67.25	109.88, 122.03, 128.22, 128.94, 129.43, 134.62, 140.64, 142.65, 144.74, 150.40, 156.72, 161.74

* In $(CD_3)_2SO$.

Table 4 Electronic spectra of the phthalocyanines

Compound	λ_{max}/nm ($10^{-4}\varepsilon$/dm^3 mol^{-1} cm^{-1})
3a^a	685 (10.68), 600 (3.2),^{b} 349 (8.4), 260 (12.7)
3b-$4H_2SO_4$^{c}	640 (4.66), 350 (4.28),^{b} 325 (5.4), 270 (6.14)^b
3c^c	635 (4.2), 391 (0.88), 327 (4.76)
4^d	673 (7.46), 650 (3.3),^{b} 602 (3.1), 330 (5.1),^{b} 263 (9.28)
5^e	717 (3.02), 677 (11.98), 647 (2.96),^{b} 607 (2.52), 420 (0.88),^{b} 333 (4.3), 229 (6.12), 202 (5.24)
6a^e	670 (18.36), 648 (4.20),^{b} 602 (3.50), 320 (54.2), 271 (6.18), 227 (5.76)
6b-$4H_2SO_4$^{c}	650 (1.92), 340 (3.28),^{b} 290 (3.80)
6c^c	668 (4.34), 630 (4.30), 307 (6.96),^{b} 273 (6.92)^b
7^e	697 (7.64), 675 (6.80), 354 (3.54),^{b} 263 (28.08)

^{a} In dimethylformamide. ^{b} Shoulder. ^{c} In water. ^{d} In Me_2SO. ^{e} In $CHCl_3$.

Table 5 Conductivity of phthalocyanines in air at room temperature

Compound	$\sigma_{d.c.}$/S m^{-1}
3a	8.4×10^{-10} 1.3×10^{-12}*
3b·$4H_2SO_4$	2.05×10^{-13}
3c	3.29×10^{-13}
4	$<10^{-13}$
5	2.16×10^{-12}
6a	4.59×10^{-12} 1.7×10^{-12}*

* In vacuum.

dichloromethane. Increasing the concentration leads to aggregation which is easily monitored by the position of the Q band which shifts to shorter wavelengths and decreases in molar absorption coefficient. The D_{2h} symmetry of the metal-free phthalocyanine is verified by the two absorptions in the visible region. The sulfonated products obtained after detosylation show aggregation even at very low concentrations. The Q bands shift 45–50 nm to higher energy from **3a** to **3b** or **3c**. Of course the solvent effect should also be taken into account because the last two products are soluble only in water.

The thermal stability of phthalocyanines **3**–**6** was determined by thermal analysis. Due to the high thermal stability of the phthalocyanine core, cleavage of the substituent macrocycles takes place first and then the main decomposition occurs above 400 °C.

Electrical Conductivity.—The *N*-tosylated derivatives of phthalocyanines **3**–**6** and the SO_3H and SO_3Na derivatives of the copper phthalocyanine **3b** and **3c** were investigated with respect to their d.c. conductivity. The data obtained for compressed microcrystalline powders are shown in Table 5. Although conductivity values obtained from high-quality single crystals or Langmuir–Blodgett films would be more desirable such samples could not have been prepared from these phthalocyanines and identical treatments during the sample preparation steps decrease the influences caused by extrinsic parameters such as particle size and purity.

The first observation from Table 5 is that the σ values are of the order of 10^{-12} S m^{-1} which is in accordance with the expectations for bulky peripheral substituents.[4,19] Secondly, the comparable values encountered with different first-row transition-metal ions show the small effect of changing the core metal ion. Thirdly, detosylation of aza functions and addition of SO_3H or SO_3Na groups to the macrocyclic substituents simultaneously lowers the conductivity by a factor of 10^{-1}. In the case of peripheral sulfo groups, the conductivity was reported to be somewhat higher than that for the unsubstituted case and was explained as due to the ionic conductivity of $SO_3HSO_3^-$ groups.[20] In the present case the bulky macrocyclic substituent should also prevent such interaction of sulfo groups.

The behaviour of compound **3a** *in vacuo* and in dry air is especially important for some applications (*e.g.* gas sensors). The increase in conductivity in dry air is a result of partial reversible oxidation.

Experimental

Routine IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer as KBr pellets, electronic spectra on a Varian DMS 90 spectrophotometer. Elemental analysis was performed by the Instrumental Analysis Laboratory of TUBITAK Gebze Research Center. Thermogravimetric analysis were run on a DuPont type 990 differential thermo-instrument at 10 °C min^{-1} in a nitrogen flow (100 cm^3 min^{-1}). Proton and ^{13}C NMR spectra were recorded on a Bruker 200 MHz spectrometer. Conductivity measurements were carried out as gold–metal phthalocyaninate–gold sandwiches prepared by coating the pressed pellets with gold using a Varian R & D 3119 coater.[21] 1,1′-Oxybis(ethyleneoxy)bis(2-nitrobenzene) and its amino derivative were synthesised according to the reported procedure.[22]

Syntheses.—*1,1′-Oxybis(ethyleneoxy)bis(2-toluene-*p*-sulfonylaminobenzene)* **1b**. 1,1′-Oxybis(ethyleneoxy)bis(2-aminobenzene) **1a** (22.55 g, 78 mmol) was dissolved in pyridine (63 cm^3) and powdered toluene-*p*-sulfonyl chloride (29.74 g, 156 mmol) was added portionwise over 2 h to the stirred and ice-cooled solution. Stirring and cooling was continued for 1.5 h and then the mixture was poured onto ice (300 g) and diluted with water (300 cm^3). The precipitated ditosylate was filtered off and washed with water (500 cm^3). Recrystallization from EtOH (300 cm^3) gave the pure ditosylate. Yield: 41.34 g (89%). ν_{max} 460–480, 520, 540–560, 680, 710, 800–820, 920–960, 1060, 1100, 1120, 1140, 1160, 1260, 1300, 1340, 1400–1420, 1460, 1500, 1600, 2840–2860, 3240 and 3420 cm^{-1}.

Compound **2a**. Compound **1b** (12 g, 20 mmol) was dissolved in EtOH (330 cm^3) containing finely ground anhydrous K_2CO_3 (6.6 g, 47.7 mmol) and refluxed for 1 h. A solution of 1,2-dibromo-4,5-bis(bromomethyl)benzene (10.4 g, 24.66 mmol) in EtOH (170 cm^3) was added dropwise over a period of 4 h. After the reaction mixture had been refluxed for 48 h the solvent was distilled off and the yellow residue dissolved in CH_2Cl_2 (50 cm^3) and filtered. The filtrate was washed with water (3 × 50 cm^3) to separate any inorganic residue, dried with sodium sulfate, filtered, and evaporated to dryness. The yellowish residue was crystallized from toluene. Yield: 8 g (47%). M.p. 235–238 °C. ν_{max} 560–580, 630, 660, 700, 720, 740, 820, 840, 900, 940, 1080, 1100, 1120, 1160, 1220, 1260, 1280, 1340, 1450, 1500, 1600, 2840–2860, 3060 and 3420 cm^{-1}.

Compound **2b**. Compound **2a** (10 g, 11.7 mmol), CuCN (3.22 g, 36 mmol) and anhydrous dimethylformamide (51 cm^3) were refluxed at 175–180 °C for 9 h under argon. After cooling to room temperature the dark brown mixture was poured into aqueous NH_4OH (25%) (250 cm^3) and air was passed through the solution for 24 h. It became dark blue and a green precipitate formed. The reaction mixture was filtered, washed with water until the filtrate was neutral, washed with cold EtOH, filtered through Celite and sand and then dried. The precipitate together with Celite and sand was placed in the thimble of a Soxhlet extractor and extracted for 72 h with toluene. The solvent was evaporated under vacuum and the residue was dissolved in CH_2Cl_2 (15 cm^3). Reprecipitation with EtOH and filtration gave the product. This compound is soluble in dichloromethane, chloroform and toluene. Yield: 5.5 g (63%). ν_{max} 660, 740, 800, 820, 860, 880, 900, 940, 1100, 1120, 1180, 1220, 1260–1280, 1360, 1400, 1460, 1500, 1600, 2220, 2840–2860 and 3040 cm^{-1}.

Copper phthalocyanine **3a**. A mixture of compound **2a** (3 g, 3.50 mmol), CuCN (0.825 g, 9.22 mmol) and dry tmu (3.75 cm^3) was heated and stirred at 185–190 °C under argon in a sealed glass tube for 8 h. After cooling to room temperature the dark green mixture was diluted with EtOH (12 cm^3) and the crude product was precipitated. It was filtered off and washed with hot ethanol to remove the unreacted organic material. The precipitate was refluxed with a solution of NaCN in water–ethanol (1:2) (five times) to remove the excess of CuCN and filtered off. Then the dark green product was washed with water, EtOH and diethyl ether and dried. Yield: 1.4 g (52.6%). It is slightly soluble only in dimethyl formamide. ν_{max} 560–580, 660, 720, 760, 820, 1060, 1100, 1160, 1260, 1280, 1340, 1460, 1500, 1600, 2840–2860 and 3420 cm^{-1}.

Metal phthalocyanines **4**–**7**. *Compound* **4**. A mixture of compound **2b** (2 g, 2.67 mmol), $NiCl_2$ (0.195 g, 1.5 mmol) and anhydrous quinoline (2 cm^3) was heated and stirred at 220 °C for 8 h under argon in a round-bottomed flask. The resulting green suspension was cooled. After filtration the product was dissolved in dimethylformamide (10 cm^3) and the solution was added dropwise to hot ethyl acetate (50 cm^3) with stirring. The precipitate formed was filtered off, washed with hot ethyl acetate then with diethyl ether and dried. Yield: 0.350 g (17%). This compound is soluble in dimethyl sulfoxide. ν_{max} 560–580, 660, 720, 760, 800, 810, 840, 900, 940, 1060, 1100, 1160, 1200, 1240, 1260, 1290, 1340, 1440, 1500, 1520, 1600, 2840–2860 and 3420 cm^{-1}.

Compound **5**. A mixture of compound **2b** (2.5 g, 3.34 mmol), $Zn(O_2CMe)_2$ (0.225 g, 1.22 mmol) and anhydrous quinoline (2.2 cm^3) was heated and stirred at 195–200 °C for 11 h under argon. After cooling to room temperature the dark green mixture was diluted with EtOH (10 cm^3) and filtered. The product was washed (five times) with EtOH and filtered. The dark green precipitate was chromatographed on neutral Al_2O_3 and eluted with dichloromethane–ethanol (100:1). Yield: 0.450 g (18%). This compound is soluble in chloroform and dichloromethane. ν_{max} 560–580, 660, 720, 760, 800, 820, 840, 900, 940, 1020, 1060, 1100, 1180, 1260, 1300, 1460, 1500, 1600, 2840–2860 and 3420 cm^{-1}.

Compound **6a**. A mixture of compound **2b** (3 g, 4.00 mmol), $CoCl_2$ (0.150 g, 1.15 mmol) and ethylene glycol (9.9 cm^3) was heated and stirred at 210–220 °C for 9 h under argon. After cooling to room temperature the reaction mixture was treated with EtOH (60 cm^3) and then the crude product was washed with water and EtOH to remove the unreacted organic material. The dark blue product was dried with diethyl ether and chromatographed on neutral Al_2O_3 with dichloromethane–ethanol (100:1) as eluent. Yield: 0.400 g (13%). This compound is soluble in chloroform and dichloromethane. ν_{max} 560–580, 660, 720, 760, 800, 820, 840, 900, 940, 1060, 1100, 1160, 1200, 1260, 1280, 1340, 1440, 1500, 1600, 2840–2860 and 3420 cm^{-1}.

Compound **7**. A mixture of compound **2b** (3 g, 4.00 mmol), PbO (0.225 g, 1.00 mmol) and 1-chloronaphthalene (1 cm^3) was heated and stirred at 210–220 °C for 9 h under argon. After cooling to room temperature the reaction mixture was treated with EtOH (15 cm^3) and filtered. The dark green precipitate was chromatographed on neutral Al_2O_3 with dichloromethane–ethanol (100:1). Yield: 0.300 g (10%). This compound is soluble in chloroform and dichloromethane. ν_{max} 590, 660, 720, 760, 820, 920–940, 1080, 1100, 1180, 1280, 1300, 1360, 1460, 1500, 1600, 2840–2860 and 3420 cm^{-1}.

Detosylation of metal phthalocyanines with H_2SO_4. Compound **3a** (4 g, 1.30 mmol) was treated with concentrated H_2SO_4 (44 cm^3) at 125–130 °C for 6 h. After cooling it was poured into cold ethanol (600 cm^3) and centrifuged. The blue precipitate was stirred in EtOH to remove the excess of H_2SO_4 and centrifuged. After dissolving in the minimum amount of water (*ca.* 5 cm^3), reprecipitation was carried out from the blue solution by addition of ethanol (15 cm^3) and centrifuging. The product **3b** was dried with diethyl ether. Yield: 2 g (53%). It is soluble in water. ν_{max} 540, 600, 700, 720, 800, 920, 1040, 1120, 1200, 1260, 1440, 1500, 1600, 2840, 2860–2880 and 3420 cm^{-1}.

In order to obtain the sodium sulfonate derivative, **3b** (0.100 g, 0.035 mmol) was heated in concentrated $HClO_4$ (5 cm^3) at 80 °C for 2 h and filtered. After cooling, the solution was poured into cold EtOH (20 cm^3) and centrifuged. The blue precipitate was stirred in EtOH to remove the excess of $HClO_4$ and separated by centrifugation. It was dissolved in water (5 cm^3) and the pH raised to 12 with 2 mol dm^{-3} NaOH solution. The product **3c** was precipitated by addition of ethanol and filtered off, washed with ethanol and then with diethyl ether and dried. Yield: 0.025 g (27%). It was soluble in water. ν_{max} 540, 600, 700, 720, 800, 920, 1040, 1120, 1200, 1260, 1360, 1400, 1440, 1500, 1600, 2840–2860 and 3420 cm^{-1}.

Under similar conditions compound **6a** was detosylated to **6b** and **6c** with yields of 66 and 27% respectively.

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Received 10*th March* 1992; *Paper* 2/01305C