The synthesis of phthalocyanines at room temperature

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Condensation of 4-substituted phthalonitriles with lithium 2-*N*,*N*-dimethylaminoethoxide in 2-*N*,*N*-dimethylaminoethanol gives a non-statistical mixture of tetrasubstituted phthalocyanines at room temperature or lower while 3-substituted phthalonitriles similarly condense with lithium octan-1-olate in octan-1-ol giving 1,8,15,22-tetrasubstituted phthalocyanines as pure isomers.

Classically, phthalocyanines (Pcs) have been prepared by high temperature (200–300 °C) fusion methods from phthalic anhydride or its derivatives[1] or by condensation of phthalonitriles with lithium pentan-1-olate in refluxing pentan-1-ol (135 °C).[2,3] 1,3-Diiminoisoindolines, prepared from phthalonitriles, are readily condensed to phthalocyanines in refluxing 2-*N*,*N*-dimethylaminoethanol (DMAE) (135 °C).[4,5] Lower temperature synthesis of phthalocyanines in refluxing butan-1-ol (80 °C) using DBU[6,7] as a base is also common. Other low temperature synthesis include the use of 1,3,3-trichloroisoindolines,[8] 1-imino-3-methylthio-6-neopentoxyisoindoline,[9] or UV methods[10] but all give phthalocyanines in low yields, use complex apparatus or require poorly accessible starting materials.

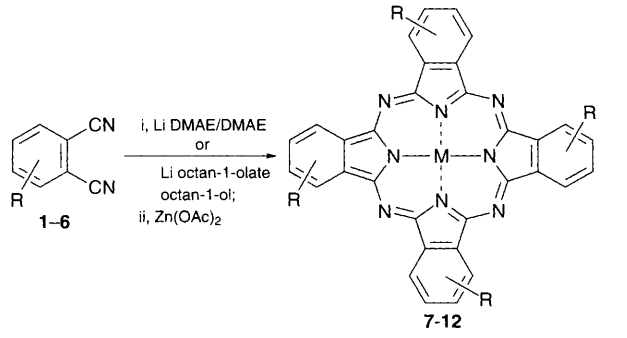
Condensation of 4- and 3-substituted phthalonitriles typically give a mixture of four different regioisomers.[11] It has recently been shown that bulky substituents in 3-substituted phthalonitriles promotes single isomer formation[12] upon condensation at 75 °C in octan-1-ol.

The development of a routine phthalocyanine synthesis at room temperature or lower would be important in that temperature sensitive substituents on the precursor phthalonitrile could be used, the extent of impurities formed at higher temperatures could be reduced, impurities which are difficult to remove could thus be eliminated, and the possibilities of forming single isomer phthalocyanines incorporating a wide variety of substituents would be enhanced.

In condensations in our laboratory using diminoisoindolines in DMAE, we had noticed that phthalocyanine formation begins to occur at a temperature as low as 90 °C even though the standard procedure is accomplished at 135 °C. We thought of preparing the alkoxide of this solvent with lithium metal and using this alkoxide in phthalocyanine formation, a seeming trivial modification of existing protocol but one that has important ramifications. We subsequently showed that lithium octan-1-olate in octan-1-ol was also successful for phthalocyanine formation at room temperature but that lithium pentan-1-olate in pentan-1-ol or lower molecular weight alkoxides in lower alcohols did not give phthalocyanines at lower temperatures in accordance with the literature.[1,2] Thus, condensation of phthalonitrile **1**, 4-neopentoxyphthalonitrile[13] **2** or 4-nitrophthalonitrile **3** in lithium DMAE at 50, 20 or 3 °C and 3-neopentoxyphthalonitrile[14] **4**, 3-*p*-butylbenzyloxyphthalonitrile[12] **5** or 3-methoxyphthalonitrile[15] **6** in lithium octan-1-olate in octan-1-ol at 20 °C readily took place. Normal work-up of the reactions from **1–3** gave phthalocyanine **7**, 2,9,16,23-tetraneopentoxyphthalocyanine[13] **8** and 2,9,16,23-tetranitrophthalocyanine[5,16] **9**, while treatment of the reactions from **4–6** with zinc acetate gave 1,8,15,22-tetraneopentoxyphthalocyaninato zinc(II) **10**, 1,8,15,22-tetra(*p*-butylbenzyloxy)phthalocyaninato zinc(II)[12] **11** and 1,8,15,22-tetramethoxyphthalocyaninato zinc(II)[15] **12** respectively, (Scheme 1), in 8–56% yield (Table 1). The lower the temperature of the reaction, the longer time is required. A typical procedure for the low temperature synthesis is described.†

Analysis of the phthalocyanines by ^{1}H NMR spectroscopy revealed that **8** and **9** existed as a non-statistical mixture of isomers but that **10**,‡ **11** and **12**‡ were produced as pure single isomers, **10** and **12** for the first time. The ^{13}C NMR spectrum of the aromatic region of **10**† is shown in Fig. 1 and compared with that of **10** prepared at high temperature, which gave a mixture of isomers.

It had been previously assumed that the formation of a pure isomer of a 1,8,15,22-tetrasubstituted phthalocyanine was due to the steric bulk of the 3-substituent, preventing the formation of other sterically constrained regiomers.[12] It is possible that electronic effects are important in the cyclic condensation of the phthalonitrile. This idea gained some credence when condensation of the sterically less demanding **6** also yielded **12** as a single isomer. Further studies on the mechanism of low temperature phthalocyanine formation are in progress.



1,7 R = H; **2,8** R = 4-OCH_2CMe_3;
3,9 R = 4-NO_2; **4,10** R = 3-OCH_2CMe_3;
5,11 R = 3-OCH_2Ph-*p*-Bu; **6,12** R = 3-OMe;
7–9 M = H_2; **10–12** M = Zn

Scheme 1

Table 1 Low temperature preparation of phthalocyanines

Pc[a]	*T*/°C	*t*[b]	Solvent	Yield (%)
7	50	24 h	DMAE	56
7	20	24 h	DMAE	16
7	3–5	72 h	DMAE/THF	10
8	50	24 h	DMAE	36
8	20	4 d	DMAE	15
8	3–5	8 d	DMAE	10
9	20	3 d	DMAE/Dioxane	38
9	3–5	3 w	DMAE/THF	45
10	20	7 d	octan-1-ol	18
11	20	7 d	octan-1-ol	13
12	20	7 d	octan-1-ol	8

[a] Concentrations of the precursor phthalonitriles **1–3** were 250 mg ml^{-1}, while those of **4–6** were 40 mg ml^{-1}. [b] Hours (h), days (d), weeks (w).

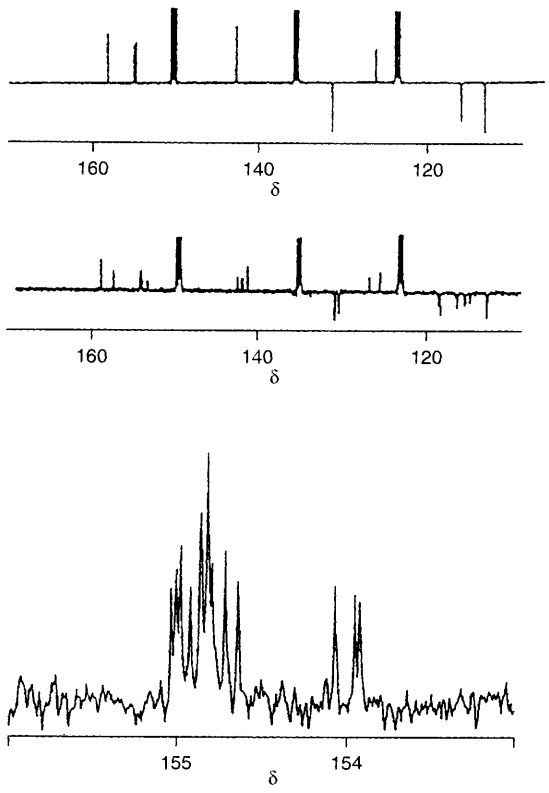


Fig. 1 ^{13}C NMR spectra of the aromatic region of the pure isomer, 1,8,15,22-tetraneopentoxyphthalocyanine **10** (top) (only two N–C–N carbon absorptions at δ 154.97 and 154.73; of **10** as a mixture of regioisomers (middle); of the internal N–C–N carbon absorptions of **10** as a mixture of regioisomers (bottom). Pyridine absorptions occur at δ 150.35, 135.91 and 123.87.

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Footnotes

† A suspension of 0.02 g of lithium in 3.0 ml of octan-1-ol was heated to 170 °C and stirred until a homogeneous solution was obtained. The solution was cooled to 20 °C and 150 mg of **4** in 1 ml of THF was added. The mixture was stirred for 7–10 d, after which excess zinc acetate was added and the mixture stirred for another 2–3 d. The reaction was quenched with methanol and water (1 : 1) and washed with methanol. The crude products were purified by column chromatography on silica gel and **10** was obtained as a blue solid in 18% yield. Recrystallization of **10** from benzene gave blue needles.

‡ Satisfactory spectroscopic data were obtained for all compounds and elemental analysis for the new single isomers **10** and **12**. *Selected spectroscopic data* for **10**: UV–VIS (THF) λ_{max}/nm (log ε) 698 (5.24), 662 (4.30), 622 (4.26) and 365 (4.12); IR ν/cm^{-1} (KBr) 3010, 2920, 2840, 2820, 1575, 1480, 1335, 1255, 1230, 1130, 1090, 1060, 1040, 1020, 800, 760 and 735; ^1H NMR (400 MHz, [$^2H_5$]pyridine) δ 9.72 (d, 4 H, *J* 7.4 Hz), 8.34 (t, 4 H, *J* 7.4 Hz), 7.76 (d, 4 H, *J* 7.8 Hz), 4.37 (s, 8 H) and 1.72 (s, 36 H); ^{13}C NMR (100.6 MHz [$^2H_5$]pyridine) δ 158.10, 154.97, 154.73, 142.85, 132.00, 126.47, 116.90, 113.25, 79.70, 33.32 and 27.35; FAB–MS for $C_{52}H_{56}N_8O_4Zn$ *m/z* (relative intensity, %) 920 (M^+, 100). For **12**: UV–VIS (THF) λ_{max}/nm (log ε) 694 (5.24), 662 (4.37), 62 (4.43) and 368 (4.37); IR ν/cm^{-1} (KBr) 3010, 2920, 2840, 2820, 1575, 1480, 1335, 1262, 1230, 1130, 1090, 1060, 1040, 1020, 800, 760 and 735; ^1H NMR (400 MHz, [$^2H_5$]pyridine) δ 9.55 (d, 4 H, *J* 8.0 Hz), 8.18 (t, 4 H, *J* 8.0 Hz), 7.69 (d, 4 H, *J* 7.9 Hz) and 4.58 (s, 8 H); ^{13}C NMR (100.6 MHz [$^2H_5$]pyridine) δ 156.85, 155.07, 154.89, 142.93, 132.03, 127.04, 117.24, 113.81 and 56.88; FAB–MS for $C_{36}H_{24}N_8O_4Zn$ *m/z* (relative intensity, %) 696 (M^+, 100).

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