

Selective Synthesis of Binuclear and Trinuclear Phthalocyanines Covalently Linked by a One Atom Oxygen Bridge

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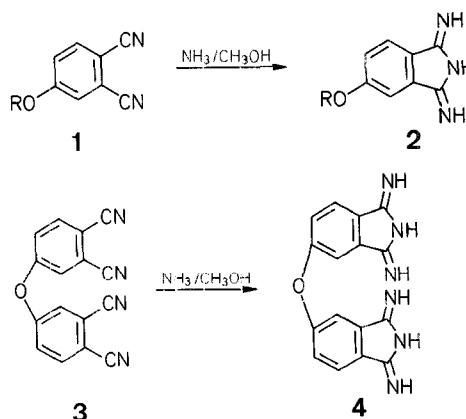
The diiminoisoindolines obtained from 4-neopentoxypthalonitrile and bis[3,4-dicyanophenyl] ether gave, in a mixed condensation reaction, binuclear and trinuclear phthalocyanines covalently linked by one atom oxygen bridges with the dimer predominating. The underivatized 4-neopentoxypthalonitrile condensed with the diiminoisoindoline of bis[3,4-dicyanophenyl] ether in a cross reaction to give the same dimer and trimeric phthalocyanines but the trimer predominated in this reaction. A cobalt derivative of bis-2-[19,16,23-trineopentoxypthalocyaninyl] ether, the binuclear phthalocyanine, was prepared. All phthalocyanines exhibited parent ions in their fast atom bombardment mass spectra.

Although the syntheses of polyphthalocyanines^{1,2}, phthalocyanines bound to polymers³, and multinuclear metallo-phthalocyanines bound through the metal ion⁴ have been

reported, it is only recently that binuclear phthalocyanines, covalently bound to each other have been described^{5,6,7}. Thus, dimeric phthalocyanines, covalently linked by two⁷, four⁷, and five^{5,6} atom bridges and their metallated derivatives have been made. In some of these reports it was noted that some phthalocyanines, suspected to be trimeric in nature were formed but these products were not completely characterized. We describe herein a phthalocyanine synthesis that preferentially forms a trinuclear phthalocyanine, compared to a binuclear phthalocyanine and a trinuclear phthalocyanine is fully characterized for the first time. In addition, the first binuclear phthalocyanine, covalently linked by a one atom bridge is described.

It has been shown that 4-neopentoxypthalonitrile (**1**) can undergo self-condensation reactions⁶ to metallated mononuclear phthalocyanines while condensation of 5-neopentoxy-1,3-diiminoisoindoline (**2**) reacts to give a metal-free mononuclear phthalocyanine^{5,6}. It was apparent to us that the reaction conditions necessary for the self-condensation of isoindoline **2** were milder than those for **1** and that the resulting reaction mixture was purer from **2** than from **1**. The *mixed* condensation of two *different* diiminoisoindolines led to a variety of metal-free binuclear phthalocyanines admixed with large amounts of mononuclear phthalocyanines and small amounts of products which appeared to be trinuclear phthalocyanines^{5,6,7}. We felt it may be possible to perform a *crossed* condensation of a phthalonitrile such as **1** with a bis-1,3-diiminoisoindoline. We believed that self-condensation of the phthalonitrile under the normal condensation conditions⁸ would be inhibited and that greater yields of binuclear phthalocyanines would be formed than in the previously described *mixed* condensations^{5,6,7}. Alternatively, a *crossed* condensation of an isoindoline such as **2** with a bisphthalonitrile may also be expected to yield binuclear phthalocyanines at the expense of higher homologs, although in this case the self-condensation of the monomer would likely give large amounts of mononuclear phthalocyanines. Although a crossed condensation had been once attempted⁹ to form an unsymmetrical phthalocyanine analog, this method had neither been elaborated nor applied to unsymmetrical phthalocyanines themselves or, of course, multinuclear phthalocyanines. Now that binuclear phthalocyanines have been prepared, characterized, and readily separated from mononuclear phthalocyanines^{5,6,7}, it becomes feasible and advantageous to attempt *crossed* condensations leading to binuclear and trinuclear phthalocyanines.

Thus treatment of bis[3,4-dicyanophenyl] ether^{6,10} (**3**) with ammonia gas^{6,8} gave the bis-1,3-diiminoisoindoline (**4**). A



binuclear phthalocyanine, covalently linked by a single atom bridge had not been previously reported and hence a *mixed* condensation of the two 1,3-diiminoisoindolines **2** and **4** was performed (Method A) by standard procedures⁵⁻⁸, giving after flash chromatography¹¹, large amounts of the monomeric 2,9,16,23-tetraneopentoxypthalocyanine (**5**)^{5,6}, some binuclear bis-2-[9,16,23-trineopentoxypthalocyaninyl] ether (**6**) and some trinuclear 2,16-bis-2'-[9',16',23'-trineopentoxypthalocyaninoxy]-9,23-dineopentoxypthalocyanine (**7**) (only one representative isomer of which is illustrated here) in modest yields and in dimer/trimer ratios of $\approx 3:1$ (Table).

condensation followed by cross condensation leading with **1** to trimer **7** as well as the simple crossed condensation forming **6**. Performing the cross condensation in the reverse sense (Method C), i. e. reaction of the bisphthalonitrile **3** with the 1,3-diiminoisoindoline **2** yielded only traces of dimer **6** and trimer **7** and the major product was simply monomer **5**. A dicobalt(II) derivative was readily prepared from **6**^{5,6}. Separation of the monomer **5** and purification of **6** and **7** was achieved as previously described by column and flash chromatography¹¹. The ultraviolet and visible spectra of **6** exhibited absorptions consistent with that previously de-

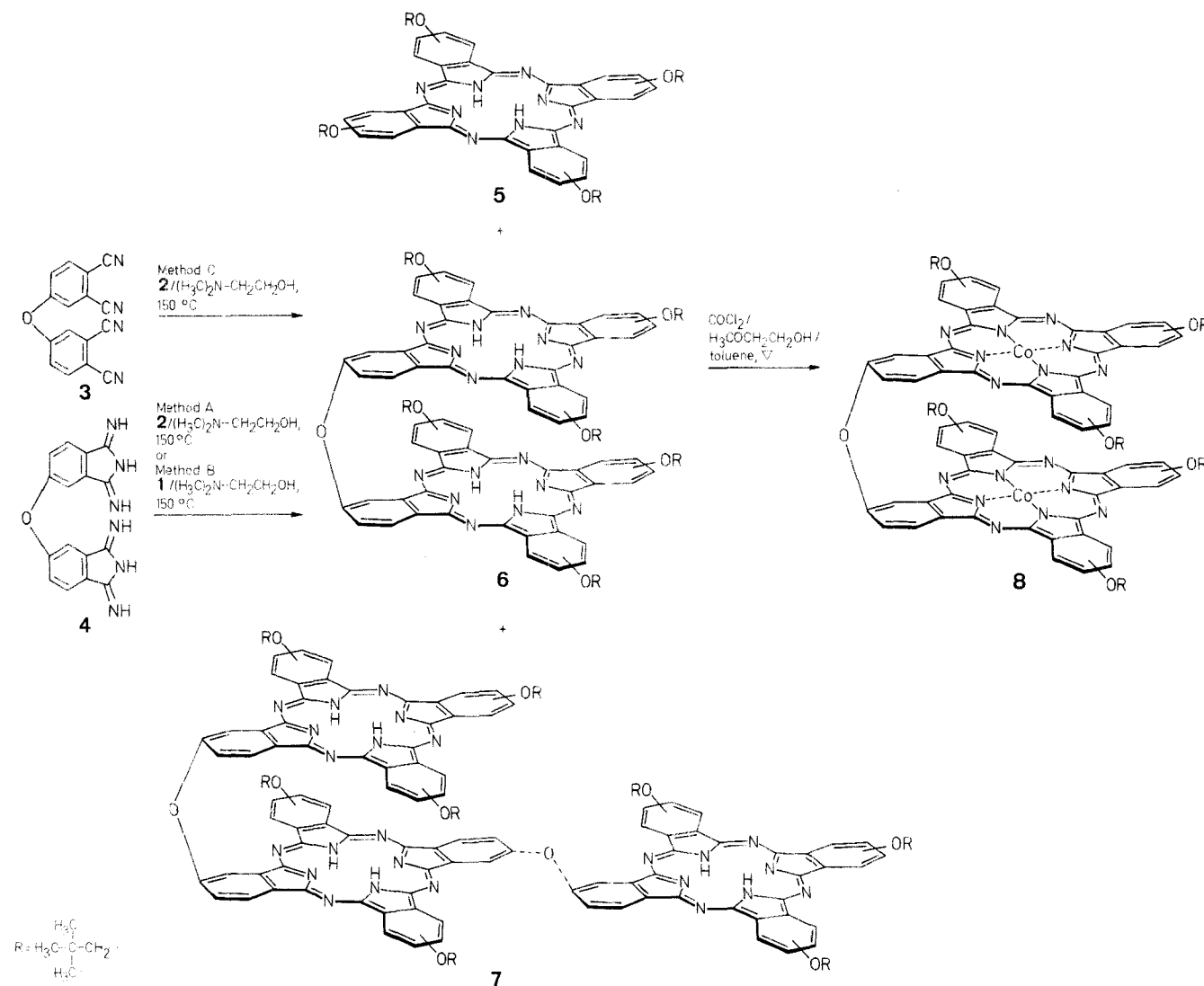


Table. Yields of Phthalocyanine Monomer, Dimer, and Trimer

Starting Materials	Method	Yield [%] of Monomer 5	Dimer 6	Trimer 7
2 + 4	A	52	11	4
1 + 4	B	49	2	6.6
2 + 3	C	36	trace	trace

On the other hand a *crossed* condensation of **4** with excess **1** under the same conditions (Method B) as the mixed condensation gave **5**, **6**, and **7** in similar total yields but in which the dimer/trimer ratio (1:3.5) was significantly altered (Table). It appears that the reactive bis-1,3-diiminoisoindoline **4** undergoes considerable self-

scribed from dimeric phthalocyanines^{5,6,7} but trimer **7** showed absorptions typical of both monomeric phthalocyanine **5** and dimer **6** indicating that $\pi - \pi$ interaction between two rings is important but that the third phthalocyanine ring is not appreciably interacting with the other two. F.A.B. mass spectroscopic⁷ data showed that **6**, **7**, and **8** all exhibited parent ions. 1H -N.M.R. spectra of **6** and **7** exhibited the presence of the N—H protons but their chemical shift of $\delta \sim -3.0$ ppm show that either conformational mobility is high on the N.M.R. time scale^{6,7} or that cofacial interactions less than 6 Å is unlikely.

In summary, a selective cross condensation reaction leads to the preferential formation of phthalocyanine trimers. A binuclear phthalocyanine, covalently linked by a one atom ether bridge is described.

Bis-2-[9,16,23-trineopentoxypthalocyaninyl] Ether (6) and 2,16-Bis-2'-[9,16,23'-trineopentoxypthalocyaninoxy]-9,23-dineopentoxypthalocyanine (7):

Method A: The two crude diiminoisoidolines **2** and **4** obtained from 4-neopentoxypthalonitrile (**1**; 4.9 g, 22.9 mmol) and bis-[3,4-dicyanophenyl] ether (**3**; 224 mg, 0.83 mmol), respectively, are heated at 150°C (oil bath) in 2-*N,N*-dimethylaminoethanol (25 ml) for 60 h under an argon atmosphere. After cooling to room temperature, the mixture is diluted with water (150 ml) and the blue coloured residue was filtered and washed thoroughly with water (30 × 50 ml) until the filtrate was colourless. The crude product (5.4 g) is purified by flash chromatography using a 5 cm wide column packed with silica gel 12 cm high. The dark blue-green product is preadsorbed on silica and eluted with toluene (1000 ml) to give the monomeric 2,9,16,23-tetraneopentoxypthalocyanine (**5**); yield: 2.44 g. Further elution with toluene (800 ml) yields a fraction consisting largely of monomer and traces of dimer. This fraction is not further purified. Further elution with toluene (2000 ml) and toluene/2-methoxyethanol (1300 ml; 100:1) yields, after solvent evaporation, a mixed monomer dimer fraction (210 mg). Continued elution with toluene/2-methoxyethanol (200 ml; 100:1) gives an additional blue-green fraction consisting of dimer and trimer. The monomer/dimer fraction is purified by flash chromatography on a smaller column 3 cm wide. Elution with toluene removes the monomer (106 mg). Thus the total yield of monomer **5** is 2.55 g (52%). Further elution with toluene/2-methoxyethanol (100:1) yields the dimer **6** (74.6 mg). The dimer/trimer fraction is purified by repetitive flash chromatography. Elution with toluene/2-methoxyethanol (100:1) yields further dimer **6** (68.4 mg) and trimer **7** (47 mg). The combined dimer **6** (143 mg) is washed with methanol to remove very minor fluorescent impurities (detected by T.L.C.) leaving very pure bis-2-[9,16,23-trineopentoxypthalocyaninyl] ether (**6**); yield: 140 mg (11%).

$C_{94}H_{94}N_{16}O_7$ calc. C 72.38 H 6.07 N 14.37
(1559.9) found 72.15 6.31 13.96

M.S.: m/e (relative intensity) = 1561.8 (46%), 1560.8 (78%), 1559.8 (100%), 1558.8 (M^+ , 64%).

I.R. (KBr): ν = 750 (m, C—H_{arom}); 1020 (vs, N—H); 1100 (s, C—O); 1245 (s, C—O); 1620 (vs, C=C); 3300 cm^{-1} (w, N—H).

U.V. (CH₂Cl₂): λ_{max} (log ϵ) = 696 (5.13); 666 (5.23); 640 (5.25); 616 (sh) (5.20); 388 (5.04); 336 nm (5.19).

¹H-N.M.R. (CDCl₃): δ = -2.8—-1.3 (vbr N—H); 0.8–1.5 (m, C—CH₃); 3.6–4.5 ppm (m, CH₂—O).

¹³C-N.M.R. (CDCl₃): δ = 27.0 (C—CH₃); 32.0 (C—CH₃); 78.0 (CH₂—O); 104.9; 117.7; 123.0; 161.1 ppm (C_{arom}).

The trimer fraction (47 mg) is washed with methanol and acetone to remove green impurities moving closely behind the trimer on T.L.C. leaving 2,16-bis-2'-[9',16',23'-trineopentoxypthalocyaninoxy]-9,23-dineopentoxypthalocyanine (**7**); yield: 39 mg (4%). Trimer **7** is then purified by vacuum liquid chromatography (V.L.C.)¹² and finally by flash chromatography to yield a very dark blue, shining solid.

$C_{136}H_{130}N_{24}O_{10}$ calc. C 72.26 H 5.80 N 14.87
(2260.7) found 72.17 6.09 14.74

M.S.: m/e (relative intensity) = 2261 (57%); 2260 (100%); 2259 (M^+ , 86%); 2258 (76%); 2257 (54%).

I.R. (KBr): ν = 750 (m, C—H_{arom}); 1020 (vs, N—H); 1100 (s, C—O); 1245 (s, C—O); 1620 (vs, C=C); 3300 cm^{-1} (w, N—H).

U.V. (CH₂Cl₂): λ_{max} (log ϵ) = 702 (5.16); 672 (5.18); 642 (5.02); 614 (sh) (4.89); 388 (4.89); 340 nm (5.16).

¹H-N.M.R. (CDCl₃): δ = -3.3—-1.8 (vbr, N—H); 0.8–1.5 (m, C—CH₃); 3.4–4.2 ppm (m, CH₂—O).

Method B: The 4-neopentoxypthalonitrile (**1**; 6.0 g, 28.0 mmol) and the isoindoline **4** obtained from bis[3,4-dicyanophenyl] ether (**3**; 284 mg, 1.05 mmol) respectively undergo a *crossed* condensation under conditions identical as before. Purification as before gives

2.94 g (49%) of monomer **5**, 32.6 mg (2%) of dimer **6**, and 78.3 mg (6.6%) of trimer **7**.

Method C: The isoindoline **2** obtained from 4-neopentoxypthalonitrile (**1**; 6.0 g, 28.0 mmol) and bis[3,4-dicyanophenyl] ether (**3**; 272 mg, 1.01 mol) respectively were heated at 150°C (oil bath) in 2-*N,N*-dimethylaminoethanol (30 ml) for 60 h under an argon atmosphere. Using an identical work-up as before, this reaction gives 2.18 g (36%) of the monomeric 2,9,16,23-tetraneopentoxypthalocyanine (**5**) and only traces of dimer **6** and trimer **7**.

Bis-2-[9,16,23-trineopentoxypthalocyaninylcobalt (II)] Ether (8):

A mixture of bis-2-[9,16,23-trineopentoxypthalocyaninyl] ether (**6**; 40 mg, 0.026 mmol) and anhydrous cobalt (II)chloride (83 mg, 0.64 mmol) in a 1:3 mixture of 2-methoxyethanol/toluene (13 ml) is refluxed under argon for 18 h. The solution is cooled and purified by flash chromatography by direct application of the crude reaction product to the column. Elution with toluene gives, after solvent evaporation, a dark, blue, shining solid (40 mg) which is washed with acetone to remove some very minor fluorescent impurities (detected by T.L.C.) leaving pure **8**; yield: 31 mg (73%).

$C_{94}H_{90}Co_2N_{16}O_7$ calc. C 67.46 H 5.42 N 13.39 Co 7.04
(1673.7) found 66.93 5.88 13.36 6.94

M.S.: m/e (relative intensity) = 1674.6 (70%); 1673.6 (100%); 1672.6 (M^+ , 68%).

I.R. (KBr): ν = 750 (m, C—H_{arom}); 1100 (vs, C—O); 1245 (vs, C—O); 1620 cm^{-1} (vs, C=C).

U.V. (*o*-dichlorobenzene): λ_{max} (log ϵ) = 680 (4.93); 650 (4.83); 330 (4.93); 300 nm (4.94).

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- Griffith, J. R., O'Rear, J., Walton, T. R. in: *Advances in Chemistry Series*, Vol. 142, Platzer, N. A. J., Ed., American Chemical Society, Washington, 1975, p. 458.
- Marullo, N. P., Snow, A. W. *Am. Chem. Soc. Symposium Series* **1982**, 14, 325.
- Keller, T. M. *U.S. Patent* 4 408 035, (1984); *C.A.* **1984**, 100, 77 562.
- Snow, A. W., Griffith, J. R., Marullo, N. P. *Macromolecules* **1984**, 17, 1614.
- Hall, T. W., Greenberg, S., McArthur, C. R., Khouw, B., Leznoff, C. C. *Nouv. J. Chim.* **1982**, 6, 653.
- Hirabaru, O., Nakase, T., Hanabusa, K., Shirai, H., Takemoto, K., Hojo, N. *J. Chem. Soc. Chem. Commun.* **1983**, 481.
- Achar, B. N., Fohlen, G. M., Parker, J. A. *J. Polym. Sci. Polym. Chem. Ed.* **1983**, 21, 1025.
- Shirai, H., Higaki, S., Hanabusa, K., Kondo, Y., Hojo, N. *J. Polym. Sci. Polym. Chem. Ed.* **1984**, 22, 1309.
- Hanack, M., Metz, J., Pawlowski, G. *Chem. Ber.* **1982**, 115, 2836.
- Metz, J., Pawlowski, G., Hanack, M. *Z. Naturforsch. Teil B* **1983**, 38, 378.
- Dirk, C. W., Inabe, T., Schoch, Jr., K. F., Marks, T. J. *J. Am. Chem. Soc.* **1983**, 105, 1539.
- Tomilova, L. G., Chernykh, E. V., Ioffe, N. T., Luk'yanets, E. A. *Zh. Obshch. Khim.* **1983**, 53, 2594.
- Leznoff, C. C., Greenberg, S., Marcuccio, S. M., Minor, P. C., Seymour, P., Lever, A. B. P., Tomer, K. B. *Inorg. Chim. Acta* **1984**, 89, L35.
- Leznoff, C. C., Marcuccio, S. M., Greenberg, S., Lever, A. B. P., Tomer, K. B. *Can. J. Chem.* **1985**, 63, 623.
- Marcuccio, S. M., Svirskaya, P. I., Greenberg, S., Lever, A. B. P., Leznoff, C. C., Tomer, K. B. *Can. J. Chem.* **1985**, 63, 2057.
- Brach, P. J., Grammatica, S. J., Ossanna, O. A., Weinberger, L. *J. Heterocyclic Chem.* **1970**, 7, 1403.

- ⁹ Elvidge, J.A., Barot, N.R. in: *The Chemistry of Double-Bonded Functional Groups*, Part 2, Patai, S., Ed., John Wiley & Sons, London, 1977, p. 1167.
Haddock, N.H., Woods, J.C. *British Patent* 762 783, (1956), Imperial Chemical Industries Ltd.; *C.A.* **1957**, 51, 12 981.
- ¹⁰ Siegl, W.O. *J. Heterocyclic Chem.* **1981**, 18, 1613.
- ¹¹ Still, W.C., Kahn, M., Mitra, A. *J. Org. Chem.* **1978**, 43, 2923.
- ¹² Targett, N.M., Kilcoyne, J.P., Green, B. *J. Org. Chem.* **1979**, 44, 4962.