

THE SYNTHESIS OF A SOLUBLE,
UNSYMMETRICAL PHTHALOCYANINE
ON A POLYMER SUPPORT

Clifford C. Leznoff and Tse Wai Hall

Department of Chemistry, York University, Downsview, Ont., Canada M3J 1P3

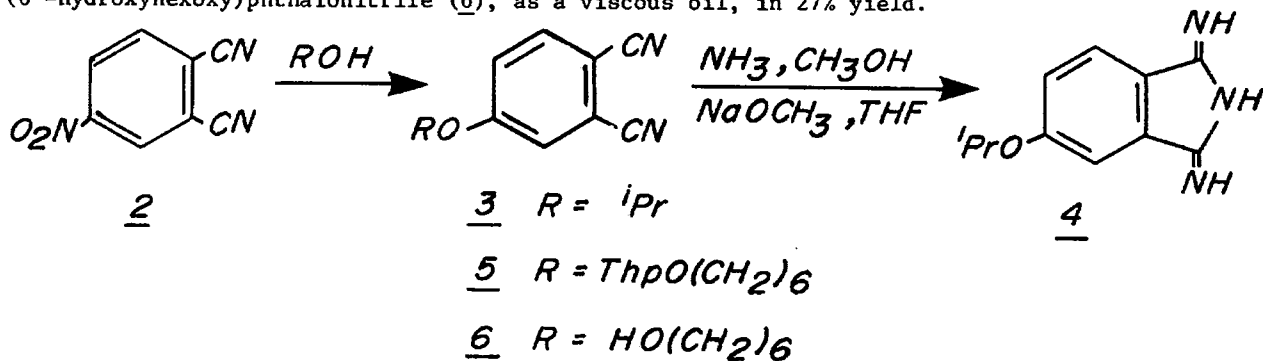
SUMMARY: A 1% crosslinked divinylbenzene-styrene copolymer was used in the preparation of the unsymmetrical 2-(6'-hydroxyhexoxy)-9,16,23-triisopropoxyphthalocyanine, soluble in common organic solvents.

Interest in phthalocyanines as potential photocatalysts for energy conversion processes is widespread.¹ Most phthalocyanines used in these studies are simple metallophthalocyanines, symmetrical tetra or even octasubstitutedphthalocyanines.² The possibility of using chemically modified electrodes³ by attaching unsymmetrical phthalocyanines to them exclusively at one linkage prompted us to seek methods to prepare unsymmetrical phthalocyanines containing a single functional group handle.

The difficulties encountered in synthesizing an unsymmetrical phthalocyanine are twofold. Firstly, condensation of two different phthalonitriles in a standard synthesis^{4,5} could give a statistical distribution of mono, di, tri and tetrasubstitutedphthalocyanines.⁶ Secondly, the notorious insolubility of phthalocyanines in organic solvents such as toluene, methylene chloride, or ether precludes chromatographic separations of the statistical mixtures obtained. We have shown⁷ that we can solve the statistical problem described above by using insoluble polymer supports for the syntheses of the related unsymmetrical meso-tetraarylporphyrins and we felt that solid phase technology^{8,9} could be used advantageously in the synthesis of an unsymmetrical phthalocyanine. Although 4-tert-butylphthalonitrile (1) can be used to prepare soluble symmetrical tetra-tert-butylphthalocyanines^{10,11}, it transpires that 1 can only conveniently be prepared in small quantities by the reported method¹⁰ and was unsuitable for our purposes. A new 4-substitutedphthalonitrile leading to a new soluble phthalocyanine was thus required.

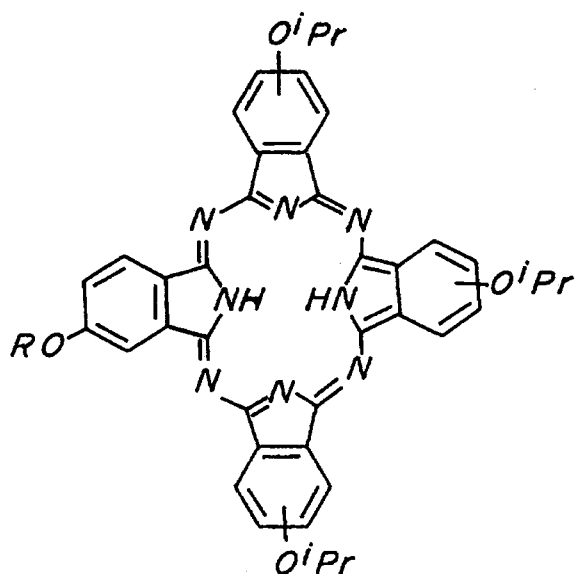
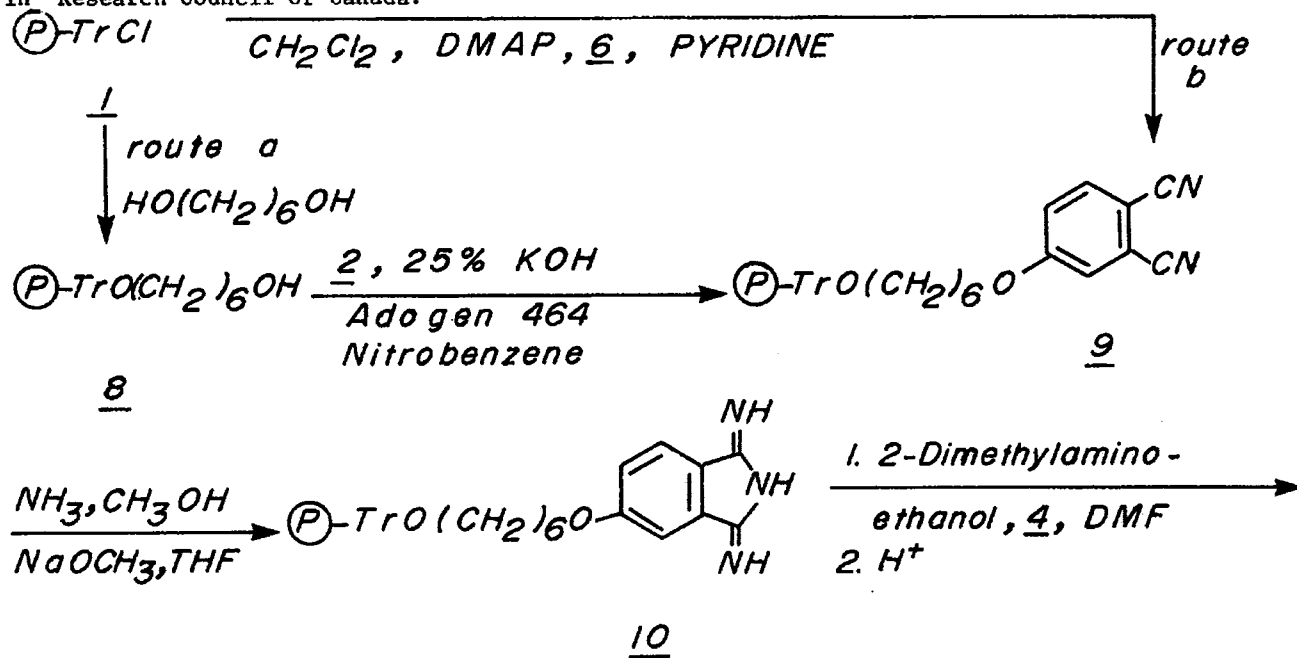
Treatment of 4-nitrophthalonitrile (2) with isopropanol and potassium carbonate¹² gave 4-isopropoxyphthalonitrile (3), mp 58-58.5° in 39% yield. Conversion of 3 with ammonia gave

the diiminoisoindoline 4, which was not purified but used directly in subsequent condensations.^{4,5} In a similar but modified procedure, 17 mmol of 2 reacted with 17 mmol of the mono-tetrahydropyranyl ether of 1,6-hexanediol and powdered KOH in freshly distilled dimethylformamide (DMF) at 100° for 15 hr to give intermediate 5, which on hydrolysis with 4N HCl gave 4-(6'-hydroxyhexoxy)phthalonitrile (6), as a viscous oil, in 27% yield.



For the mixed condensation a polymer-bound diiminoisoindoline was required. This compound was prepared in two ways. Polymer-bound trityl chloride (7)^{8,9,13} was converted to the polymer-bound monotrityl ether of 1,6-hexanediol (8)¹³. Treatment of 7.3g of 8 with 25% KOH and Adogen 464 in nitrobenzene at 60° for 22 hr in the presence of excess 2 (7.5g) in a modification of Fréchet's three phase reaction¹⁴ yielded 7.3g of the polymer-bound phthalonitrile (9). Hydrolysis of 1.0g of 9 in 30ml of 0.35 N HCl (dry gas) in dry dioxane at 20° yielded 0.26 mmol of 6 per gram of 9 by route a. Alternatively, polymer 7 reacted with 6 in pyridine, methylene chloride, and *p*-N,N-dimethylaminopyridine (DMAP) to give 9. Hydrolysis of 1.0g of 9, prepared via route b gave 0.53 mmol of 6 per gram of 9. Infrared spectroscopy (IR) (KBr) of 9 showed C≡N str. at 2240 cm⁻¹. The ¹³C NMR (polymer swollen in CDCl₃) showed absorbances at 162.0, 145.0, 117.2, 115.2, 86.3, 83.8, 69.1, 63.2, 29.8, 28.6 and 25.7 consistent with the assigned structure and with our recently described ¹³C NMR of 8.¹⁵ Conversion of 9 into the polymer-bound diiminoisoindoline (10) was accomplished as for 4 and the absorbance in the IR at 2240 cm⁻¹ for 9 had completely disappeared in 10. A suspension of 1.5g of 10 and an excess (1.24g) of 4 in a 1:1 mixture of dry DMF and 2-dimethylaminoethanol was heated to reflux under argon for 20 hr with vigorous stirring. The mixture was filtered to give a dark green filtrate and a dark green-black polymer. The filtrate on evaporation and purification by column chromatography on silica gel (ether-pet. ether, 7:3) gave 0.32g of 2,9,16,23-tetraisopropoxyphthalocyanine (11), as a dark, blue solid of related isomers, very soluble in CH₂Cl₂, CHCl₃ and even benzene. The dark green-black polymer (12) was extracted with methylene chloride in a Soxhlet extractor to remove any absorbed 11. The polymer was thus able to "fish out" the unsymmetrical phthalocyanine from a sea of polysubstituted phthalocyanines in the filtrate. Hydrolysis of 1.5g of 12 (prepared via route b) as for 9 for 51 hr and extraction of the polymer with CH₂Cl₂ in a Soxhlet extractor yielded upon evaporation 0.25g of a crude dark green residue. Chromatography on alumina with ethyl acetate-methanol (3:1) yielded 0.146g of 2-(6'-hydroxyhexoxy)-9,16,23-triisopropoxyphthalocyanine (13), as a deep, blue solid, in 24% yield as a mixture of related isomers. Compound 13 was very soluble in THF, MeOH and moderately soluble in CH₂Cl₂, CHCl₃ and acetone. Both 11 and 13 gave parent ions in their mass spectra at 746 and 804 respectively using a field

desorption probe¹⁶. The ¹H and ¹³C NMR spectra of 11, 13, and their precursors 3 and 5 were consistent with the assigned structures¹⁷. ACKNOWLEDGEMENT: This work was supported by Petroleum Research Fund of the American Chemical Society and the Natural Sciences and Engineering Research Council of Canada.



11 $R = iPr$

12 $R = \text{P-TrO(CH}_2)_6$

13 $R = \text{HO(CH}_2)_6$

References and Footnotes:

1. J.A.J. Darwent, *J. Chem. Soc. Chem. Commun.*, 805 (1980); A. Giraudeau, F.R.F. Fan and A.J. Bard, *J. Am. Chem. Soc.*, 102, 5137 (1980); R.O. Loutfy and J.H.J. Sharp, *J. Chem. Phys.*, 71, 1211 (1980).
2. W.A. Orr and S.C. Dahlberg, *J. Am. Chem. Soc.*, 101, 2875 (1979); G. Pawlowski and M. Hanack, *Syn. Commun.*, 11, 351 (1981); Z. Witkiewicz, R. Dabrowski and W. Wallawek, *Mat. Sci.* II, 39

- (1976).
3. R.W. Murray, Acc. Chem. Res., **13**, 135 (1980).
 4. P.J. Beach, S.J. Grammatica, O.A. Ossanna and L. Weinberger, J. Heterocyclic Chem., 1403 (1970).
 5. G. Pawlowski and M. Hanack, Synthesis, 287 (1980).
 6. A.H. Jackson. In The Porphyrins, Vol. I, D. Dolphin, Ed., Academic Press, N.Y. 1978, pp 365-388.
 7. C.C. Leznoff and P.I. Svirskaya, Angew. Chem. Int. Ed. Engl., **17**, 947 (1978).
 8. N.K. Mathur, C.K. Narang, and R.E. Williams, Polymers as Aids in Organic Chemistry, Academic Press, N.Y. 1980; P. Hodge, In Polymer-supported Reactions in Organic Synthesis, P. Hodge and D.C. Sherrington, Eds., Wiley, New York, 1980.
 9. J.M.J. Fréchet, Tetrahedron, **37**, 663 (1981); A. Akelah, Synthesis 413 (1981); C.C. Leznoff, Acc. Chem. Res. **11**, 327 (1978).
 10. S.A. Mikhailenko, S.V. Barkanova, O.I. Lebedev, and E.A. Luk'vanets, Zh. Obshch. Khim., **41**, 2735 (1971).
 11. A.B.P. Lever, S.R. Pickens, P.C. Minor, S. Licoccia, B.S. Ramaswamy and K. Magnell, J. Am. Chem. Soc., **103**, 6800 (1981).
 12. T.M. Keller, T.R. Price, and J.R. Griffith, Synthesis, 613 (1980).
 13. T.M. Fyles and C.C. Leznoff, Can. J. Chem., **54**, 935 (1976).
 14. J.M.J. Fréchet, Org. Coat. Plast. Chem., **42**, 268 (1980); M.J. Farrall, T. Durst, and J.M.J. Fréchet, Tetrahedron Lett., 203 (1979).
 15. A.S. Jones, C.C. Leznoff and P.I. Svirskaya, Org. Magn. Resonance, in press.
 16. D.D. Eley, D.J. Hazeldine and T.F. Palmer, J. Chem. Soc., Faraday II, **69**, 1808 (1973); D.E. Games, A.H. Jackson, and K.T. Taylor, Org. Mass Spectrom., **9**, 245 (1974).
 17. **3**: IR (KBr) 2220 cm^{-1} ; δ (CDCl_3) 7.88-7.18 (m) Ar, 4.73 (heptet, $J=6.0$) $(\text{CH}_3)_2\text{CHO}$, 1.42 (d, $J=6.0$), $(\text{CH}_3)_2\text{CHO}$; δ ^{13}C 161.10, ArC-O, (135.11, 120.29, 119.91, 117.13, 115.73, 115.28, 106.25) Ar, CN, 71.64 $(\text{CH}_3)_2\text{CHO}$, 21.48 $(\text{CH}_3)_2\text{CHO}$. **5**: IR (neat) 3400, 2200 cm^{-1} ; δ (CDCl_3) 7.83-7.13 (m) Ar, 4.10 (t, $J=6.0$) CH_2OR , 3.66 (t, $J=6.0$) CH_2OH , 2.95 (br.s), OH, 1.50 (m) $(\text{CH}_2)_4$, δ ^{13}C (CDCl_3): 162.18, ArC-O, (135.17, 119.56, 119.34, 117.36, 115.70, 115.28) Ar, CN, 69.21 $\text{CH}_2\text{O-Ar}$, 62.66 HOCH_2 , (32.49, 28.73) OCH_2CH_2 , (25.63, 25.44) OCH_2CH_2 . **11**: IR (KBr) 3280, 1620, 1240, 1100, 1090, 1010, 960 cm^{-1} ; δ (CDCl_3) 8.02-6.62 (m) Ar, 5.23-4.53 (m) $(\text{CH}_3)_2\text{CHO}$, 1.66 (d, $J=6.0$) $(\text{CH}_3)_2\text{CHO}$; δ ^{13}C (CDCl_3) 159.17 ArC-O, (147.19, 136.99, 128.20, 127.93, 123.01, 118.89, 118.61, 106.24, 105.60, Ar, C \equiv N, 70.42 $(\text{CH}_3)_2\text{CHO}$, (22.59, 21.83) $(\text{CH}_3)_2\text{CHO}$. UV (CH_2Cl_2) 706 (log e, 4.64), 670 (4.58), 640 (4.19), 608 (3.98), 388 (4.09), 342 (4.40) nm. **13**: IR (KBr) 3400, 3280, 1620, 1260, 1240, 1095, 1015 cm^{-1} ; δ ^{13}C (CDCl_3) 159.2 ArC-O, (147.0, 137.1, 123.1, 117.4, 105.8, 103.8) Ar, C \equiv N, 70.3 $(\text{CH}_3)_2\text{CHO}$, (69.3, 68.2) ArOCH_2 , 62.9 CH_2OH , (32.9, 29.6) OCH_2CH_2 , (26.1, 25.9) $\text{OCH}_2\text{CH}_2\text{CH}_2$, (26.1, 25.9) $\text{OCH}_2\text{CH}_2\text{CH}_2$, 22.5 $(\text{CH}_3)_2\text{CH}$. UV (CH_2Cl_2) 705 (log e, 4.55), 669 (4.51), 643 (4.21), 609 (4.01), 390 (4.11), 343 (4.40).