Chemistry of Heterocyclic Compounds, Vol. 31, No. 10, 1995

ORGANIC CONDUCTORS BASED ON 2,5-DIAMINO-3,4-DICYANOTHIOPHENE AND DIAMINOMALEONITRILE AND THEIR TRANSFORMATION TO NEW PHTHALOCYANINE ANALOGUES

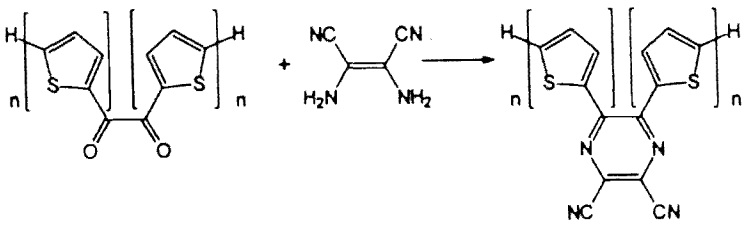
Daniel Vegh, Marian Landl, Renata Pavlovicova, Hans Kuzmany, and Peter Zalupsky

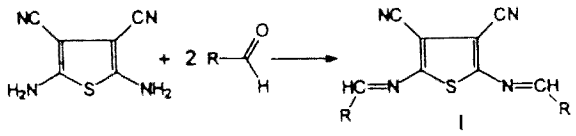
New phthalocyanine analogues were prepared based on 2,5-diamino-3,4- dicyanothiophene and diaminomaleonitrile.

In recent years there has been enormous interest in the area of conducting polymers which display a wide range of electrical conductivities [1].

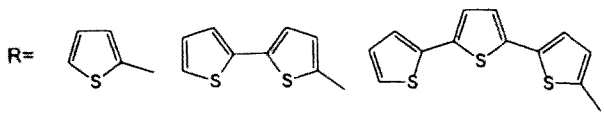
Phthalocyanines are receiving considerable attention owing to their possible use in solar energy conversion [2], as chemical sensors [3], for optical data storage [4], and for the electrocatalytic reduction of O_2 and CO_2 [5]. In addition, some phthalocyanine derivatives chelated with diamagnetic metals efficiently and selectively photoinactivate cancer cells *in vivo* [6, 7] and viruses in stored blood [8, 9]. A number of studies have focused on the attachment of metal phthalocyanines to electrode surfaces by a variety of methods [10]. The electropolymerization of metallophthalocyanines can be similarly readily carried out as the electropolymerization of metalloporphyrins [11].

Such metalloporphyrins, when electropolymerized, are expected to form polymer films with useful electrocatalytic properties. Several new derivatives of 2,5-diamino-3,4-dicyanothiophenes (I) [12, 13] (DAMCYT), as well as of the new cyclization product II of diaminomaleonitrile [14] with thenils, were prepared and the conversion of the latter to the analogues of phthalocyanines III and IV was elaborated.





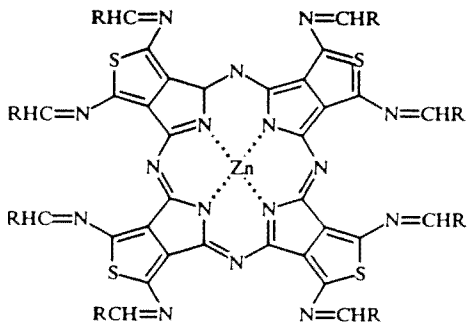
I



Department of Organic Chemistry, Slovak Technical University, Bratislava, Slovakia. Institut für Festkörperphysik der Universität Wien, Wien, Austria. Published in Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1409-1411, October, 1995. Original article submitted September 24, 1995.

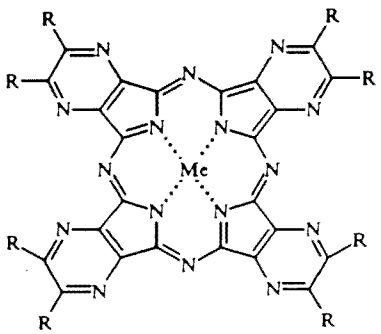
 0009-3122/95/3110-1238$12.50 ©1996 Plenum Publishing Corporation

Stable anils I were prepared from 2,5-diamino-3,4-dicyanothiophene [12, 13] and 2-thiophene and oligothiophene aldehydes [15], respectively, by heating the reactants to a temperature of 120-180°C.

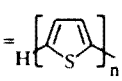


III

(R - same as for I)



IV

(Me = H, Zn, Cu; R =  , n = 1, 2, 3)

Under these conditions, both monoanils and dianils I were formed. However, the suppression of formation of monoanils could be achieved and good yields of dianils obtained when the DAMCYT:aldehyde ratio was 1:2.1 and 2 molar percent of *p*-toluenesulphonic acid was added to the reaction mixture. All the dianils are highly colored compounds. The 5,6-substituted pyrazine-2,3-dicarbonitriles II were obtained in 60-90% yields by refluxing thenils [15] with a 10% excess of diaminomaleonitrile [14] in glacial acetic acid. Both *o*-dinitriles I and II are commonly used as starting material for the synthesis of phthalocyanine analogues.

The metal-free compounds III and IV were prepared by refluxing the respective dinitrile I or II in ethanol, or ethoxyethanol with 1,8-diazabicyclo[5.4.0]undecene. The products were characterized by ^{1}H and ^{13}C NMR, UV/VIS, and IR spectroscopy.

The metallophthalocyanine analogues III and IV also resulted from a direct condensation at 170-180°C for 3-5 h of dinitriles I or II with $Zn(OAc)_2$ or $Cu(OAc)_2$. The major product of the condensation was found to be the metal-free variety of III and IV.

A higher-yield approach to metallophthalocyanine analogues III and IV is based on structures analogous to 1,3-diimino-1,3-dihydroisoindole [17] prepared by passing gaseous ammonia through a methanolic solution of dinitrile I or II. Such intermediates are used without isolation and purification in a condensation process as described above.

Compounds I-IV were characterized by elemental analysis, ^{1}H and ^{13}C NMR, UV/VIS, and IR spectra.

REFERENCES

1. M. Hanack, U. Schmid, S. Echinger, F. Teichert, and J. Hieber, Synthesis, No. 6, 634 (1993).
2. R. Jasinski, Nature, **201**, 1212 (1964).
3. J. Batey, M. C. Petty, G. G. Roberts, and D. R. Wright, Electron Lett., **20**, No. 12, 489 (1984); Chem. Abstr., **101**, 64252 (1984).
4. M. J. Cook, A. J. Dunn, S. D. Howe, A. J. Thomson, and K. J. Harrison, J. Chem. Soc. Perkin Trans. I, 2453 (1988).
5. M. R. Hempstead, A. B. P. Lever, and C. C. Leznoff, Can. J. Chem., **65**, 2677 (1987).
6. J. E. van Lier, in: Photodynamic Therapy of Neoplastic Disease, D. Kessel (ed.), CRC Press, Boca Raton, FL (1990), p. 279.
7. I. Rosenthal, Photochem. Photobiol., **53**, 859 (1991).
8. R. W. Boyle and J. E. van Lier, Synlett., No. 5, 351 (1993).
9. B. Horowitz, B. Williams, S. Rywkin, A. M. Prince, D. Pascual, Geacintov [sic], and J. Valinski, Transfusion, **31**, 102 (1991).

10. R. Jiang and S. Dong, J. Electroanal. Chem., **246**, 101 (1988), and references therein.
11. A. Bettelheim, B. A. White, and R. W. Murray, J. Electroanal. Chem., **217**, 271 (1987).
12. K. Gewald, M. Kleinert, B. Thiele, and M. Hentschel, J. Prakt. Chem., **314**, 303 (1972).
13. K. Gewald, H. Schäfer, and R. Schindler, Z. Chem., **29**, 100 (1989).
14. K. Kanakarajan and A. W. Czarnik, J. Org. Chem., **51**, 5241 (1986).
15. Y. Wei, B. Wang, W. Wang, and J. Tian, Tetrahedron Lett., **36**, 665 (1995).
16. M. Landl and D. Vegh, Synth. Commun., in press.
17. K. Kitahara, T. Asano, K. Hamano, S. Tokita, and M. Nishi, J. Heterocycl. Chem., **27**, 2219 (1990).