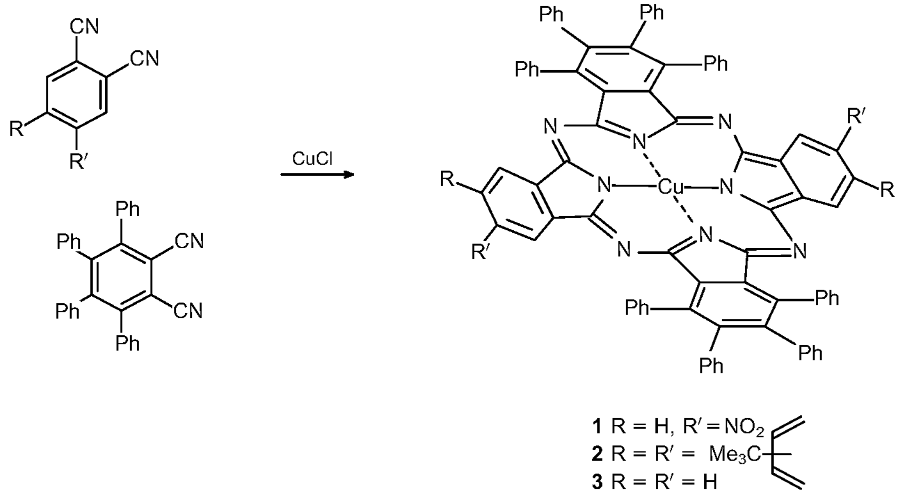
New, Non-symmetrical 2:2 Phthalocyanines. 1,2,3,4,15,16,17,18-Octaphenyl-9,23(24)-dinitrophthalo- and 1,2,3,4,19,20,21,22-Octaphenyldiphthalo-11,29(30)-di-*tert*-butyldinaphthalocyanine Copper Complexes

Viktor N. Nemykin,* Nikita B. Subbotin, Nina A. Kostromina and Sergey V. Volkov

Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine, 252680 Kiev, Ukraine.
Fax: +7 044 444 3070

The reaction between tetraphenylphthalonitrile and 4-phthalonitrile or 6-*tert*-butylnaphthalonitrile in the presence of copper(I) chloride gives a non-statistical mixture of non-symmetrical phthalocyanines from which 2:2 complexes are separated; in the reaction between substituted phthalo- and naphthalonitriles the 2:2 complex was a major product. The splitting of the Q-band in the electronic spectra depends on the differences in the electronic structure of the fragments of the non-symmetrical molecule.

The phthalocyanines are an extensive class of macrocyclic compounds, representatives of which are interesting from both theoretical and practical points of view.[1] Their extended π-system creates specific properties which are typical of this class of compounds. The introduction of functional groups in the macrocycle over a wide range modifies the electronic structure of the phthalocyanine ligand. The strongest effect is displayed on the introduction of nitro groups and linear annelation which results in the formation of polynitrophthalocyanines and 2,3-naphthalocyanines, respectively.[2] In recent years there has been an increasing interest in non-symmetrical members of this class of compounds.[3,4] One of the most interesting aspects is the influence of asymmetric replacement on the electronic absorption spectra of these compounds. On the other hand, they have significant practical interest, *e.g.*, for catalytic or highly-ordered "organic" semiconducting systems.[4,5] In an earlier communication we described the use of steric hindrance, created by bulky groups in *ortho*-dinitriles, for the formation of a non-statistical mixture of non-symmetrical phthalocyanine complexes.[6] In this article we used this strategy for the formation of new, non-symmetrical phthalocyanine copper(II) complexes possessing (except for tetraphenylisoindole) two 4-nitroisoindole **1** or 6-*tert*-butylbenzisoindole **2** fragments (2:2 complexes). Scheme 1 illustrates the synthesis of these complexes.



Scheme 1 Scheme for the synthesis of non-symmetrical phthalocyanines.

The synthesis of non-symmetrical compounds was performed at 280–300 °C in an argon atmosphere. A mixture of equimolar amounts of tetraphenylphthalonitrile[7] and 4-nitrophthalonitrile or 6-*tert*-butylnaphthalonitrile[8] with a two-fold excess of copper(I) chloride was melted in a Wood metal-bath container for 7 h. The cooled melt was treated with water, 5% aqueous HCl, 5% aqueous NH_4OH, water and was then dried. A mixture of non-symmetrical reaction products was dissolved in the minimum volume of benzene and the substances were chromatographed on silica gel using benzene as eluent. The yield of complex **1** was 14% and of complex **2**, 36%. The complex **2** is a major product of the reaction between tetraphenylphthalonitrile and 6-*tert*-butylnaphthalonitrile.

The structure of these compounds was confirmed by elemental analysis data and electronic spectroscopy.[†] The complexes synthesized are green crystalline substances (m.p. > 250 °C), which are readily soluble in many organic solvents (benzene, chloroform, DMSO, *etc.*).

The introduction of eight phenyl groups into the molecules of dinitrophthalocyanine complex **1** appreciably increases its solubility in organic solvents in comparison with tetra- and octanitrophthalocyanines.[9] We investigated the electronic absorption spectra of compounds synthesized in the range 300–900 nm (Fig. 1, Table 1). They consist of a Soret band in the range 350 nm and a Q-band in the range 600–800 nm, which has an oscillatory structure. The splitting of the Q-band results from a downturn of symmetry from D_{4h} to D_{2h} and a correspoding removal of degeneracy of the lowest unoccupied molecular orbital. The size of the split depends on the differences in electronic structure of the fragments of the non-symmetrical macrocyclic ligand: the greater the difference, the greater the splitting of the Q-band. The trend is therefore **3** < **1** < **2**, making 19, 29 and 83 nm, respectively. This series qualitatively corresponds to the influence of the substituents mentioned on the position of the Q-band in the electronic absorption spectra of symmetric phthalocyanine analogues (Table 1). The spectrum of compound **2** essentially

---

[†] *Elemental analysis.* Complex **1**: found C, 75.71; H, 3.61; N, 10.57%; calc. for $C_{80}H_{46}N_{10}O_4Cu$: C, 75.37; H, 3.64; N, 10.99%; complex **2**: found C, 82.69; H, 4.90; N, 7.66%; calc. for $C_{96}H_{68}N_8Cu$: C, 82.53; H, 4.90; N, 8.02%.

Table 1 Electronic absorption spectra of non-symmetrical phthalocyanines and their symmetrical analogues.

Compound	Solvent	λ/nm (lg ε)			Ref.
		Q		Cope	
1	Benzene	716 (4.62)	656 (4.38)		
		687 (4.67)	623 (4.31)		
2	Benzene	775 (4.59)	717 (4.25)	352 (4.21)	
		693 (4.39)	660 (3.67)		
			635 (3.94)		
			580 (3.20)		
3	THF	694 (4.91)	630 (4.62)	350 (4.70)	6
		675 (4.79)	611 (4.61)		
Bu^t_4PcCu	Toluene	677 (5.40)	646 (4.58)	346 (4.89)	2
			609 (4.65)		
			580–520sh (3.82)		
			388sh (4.65)		
Bu^t_4NcCu	Toluene	770 (5.23)	730 (4.80)	330 (5.01)	2
			687 (4.62)		
			650sh (4.26)		
			410sh (4.62)		
			380sh (4.68)		
$(NO_2)_4PcCu$	$PhNO_2$	702	682		2
			650sh		
			620sh		

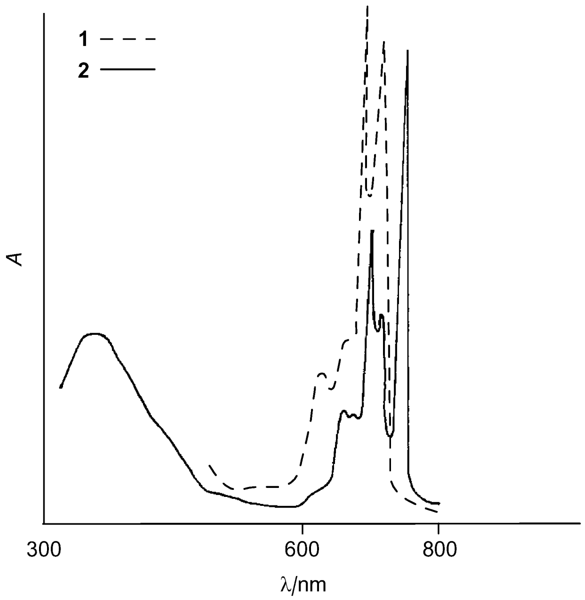


Fig. 1 Electronic absorption spectra of compounds synthesised.

represents the superposition of the spectra of phthalo- and naphthalocyanine copper complexes. Thus, at least for this complex, it is possible to assume that averaging of the electronic density in the macrocycle occurs to a lesser extent by comparison with porphyrin analogues, in which at the same asymmetry in the electronic spectra only one long wavelength band is observed.[10]

References

1 *Phthalocyanines: Properties and Applications*, eds. C. C. Leznoff and A. B. P. Lever, VCH, New York, 1989.

2 E. A. Luk'yanets, *Elektronnye spektry ftalotsianinov i rodstvennykh soedinenii (Electronic spectra of phthalocyanines and related compounds)*, Cherkassy, 1989 (in Russian).

3 N. Kobayashi, R. Kondo, S. Nakajima and T. Osa, *J. Am. Chem. Soc.*, 1990, **112**, 9640.

4 N. B. McKeown, J. Chambier and M. J. Cook, *J. Chem. Soc., Perkin Trans. 1*, 1990, 1169.

5 D. Lelievre, L. Bosio, J. Simon, J.-J. Andre and F. Bensebaa, *J. Am. Chem. Soc.*, 1992, **114**, 4475.

6 N. B. Subbotin, V. N. Nemykin and Y. Z. Voloshin, *Mendeleev Commun.*, 1993, 121.

7 R. F. Doering, R. S. Miner, L. Rothman and E. I. Becker, *J. Org. Chem.*, 1959, **23**, 520.

8 E. I. Kovshev and E. A. Luk'yanets, *Zh. Obshch. Khim.*, 1972, **42**, 696 [*J. Gen. Chem. USSR (Engl. Transl.)*, 1972, **42**, 691].

9 V. M. Negrimovsky, V. M. Derkacheva and E. A. Luk'yanets, *Zh. Obshch. Khim.*, 1989, **59**, 1688 [*J. Gen. Chem. USSR (Engl. Transl.)*, 1989, **59**, 1502].

10 M. Goutermann, in *The Porphyrins*, ed. D. Dolphin, Academic Press, New York, 1978, vol. 3, part A, pp. 1–165.

Received: Moscow, 13th September 1994
Cambridge, 15th November 1994; Com. 4/05667A