Chemistry of Heterocyclic Compounds, Vol. 31, No. 2, 1994

AGGREGATION PROPERTIES OF COPPER DIBENZOBARRELENOPHTHALOCYANINE

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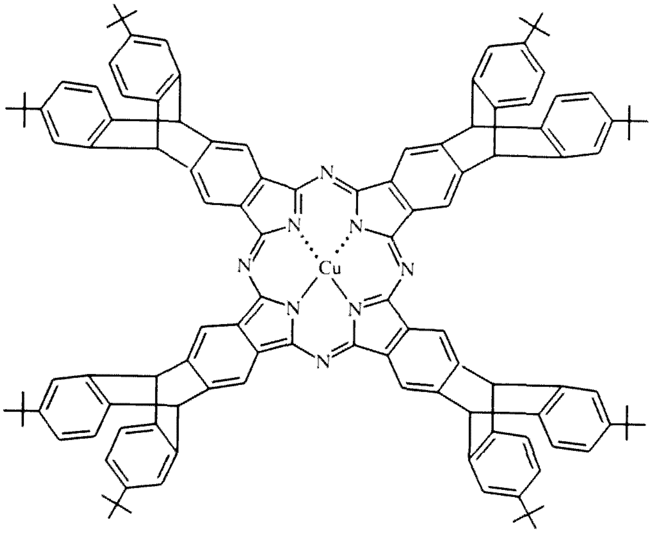
Depending on the solvent in which they are placed or from which they have been obtained, sterically hindered copper octa-tert-butyltetra-4,5-dibenzobarrelenophthalocyanines in solution and as a powder can take a monomeric form or dimer or trimer aggregate forms. In the aggregates, the molecules are disposed opposite one another around a high-order axis at an angle of 45° from equatorial displacement.

The ability of porphyrin molecules to form aggregates is known. The most studied of these are formed in solution in nonpolar solvents [1-5]. As a rule, porphyrin Cu(II) complexes form binuclear "sandwich" type molecular aggregates with the molecules placed opposite one another and displaced slightly. The value of the interplanar distance is 3.5 Å and higher.

Aggregates of phthalocyanine molecules have been studied much less (see e.g. [6-7]). In [5], the EPR method was used to show that phthalocyanines can also form dimers with different values of interionic distances and displacements depending on the nature of the peripheral substituents and the solvent used. The EPR spectra of these complexes as powders has proved uninformative.

Based on a study of electronic absorption spectra, unusual aggregates have been proposed [8] for the sterically hindered octa-tert-butyl-tetra-4,5-dibenzobarrelenophthalocyanine (I) copper compound in organic solvents.



I

In this work we have studied the EPR spectra of I in organic solvents and as a powder. Frozen solutions of I in toluene and chloroform give well resolved EPR spectra unrelated to Cu^{2+} ions with nitrogen ligands (Fig. 1a) with parameters typical of copper phthalocyanine (Table 1) [5]. After removal of solvent, the spectrum of the powder appears as a superposition of the signals for the dimer and the monomer. The ratio between them depends on the solvent and the rate of its removal. Other

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0009-3122/95/3102-0146$12.50

TABLE 1. EPR Parameters for Complexes of I in Frozen Solutions and as a Powder

Solvent	State	$G_{\parallel}$	$G_{\perp}$	A, 10^4 cm^{-1}	D, 10^4 cm^{-1}
Toluene, chloroform	Solution	2,158	—	215 A_N = 16,2 Oe	B_N =14,8 Oe
	Powder	2,16	2,04	216	
Hexane, pentane	Solution,	2,16	2,05	109	440
	Powder, slow crystallization	2,16	2,05	107	430
	Powder, rapid crystallization	2,16	2,05	218	
Acetone	Solution, monomer powder	2,16	—	217	
	Solution, dimer powder	2,16	2,05	110	430
Dichloromethane	Solution,	—	2,04	—	323
	Powder,	—	2,04	—	

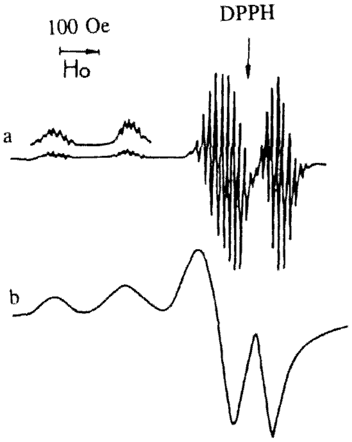

Fig. 1. EPR spectra of copper octa-tert-butyl-tetra-4,5-dibenzo-barreleno-phthalocyanine: a) in toluene at 77 K; b) as a powder at 300 K.

conditions being equal, a greater monomer content is observed in the powder obtained from toluene. A higher rate of evaporation of solvent also encourages the equilibrium to the monomer side. A distinctive feature of the powder is the additional line broadening due to a magnetic interaction of the nearby molecules. The interionic distance R_{Cu-Cu}, calculated from this line broadening, on the two point dipole model is ≥ 15 Å. In powders obtained from chloroform and acetone these distances can decrease to 11-12 Å which explains the greater spectral line broadening (Fig. 1).

EPR spectra of the dimers, virtually without contamination by the monomeric forms, are observed in pentane and hexane solutions at 77 K (Fig. 2a). In acetone, the ratio between them depends significantly on the rate of freezing. In powders obtained from these solutions, new forms could not be observed. The monomer:dimer ratio also depends on the rate of evaporation of solvent and varies over a wide range, particularly from acetone.

Based on the ratio of the parameters for the monomer and dimer complexes (Table 1), we propose a plane parallel distribution of the mutually opposite molecules from equatorial and lateral displacement in the dimer. The dimeric cation copper porphyrin radicals $(CuEP^{+})_2$ [4] give similar EPR spectra. In our case, the same structure occurs in the dimers of the neutral molecules. A distinctive feature of these spectra is the slightly lower value of the dipole–dipole splitting parameter D which can be explained by an increase in the R_{Cu-Cu} distance. In the two point dipole model R_{Cu-Cu} is 4.1 Å for compound I whereas it is 4.0 Å for $(CuEP^{+})_2$ [4, 9]. Based on the steric distribution of spin density in the sixteen point approximation [5] these distances become 3.6 and 3.5 Å respectively.

In frozen dichloromethane solution the spectrum shown in Fig. 2b is seen. A feature is the presence of two transitions placed symmetrically along the monomer G , a strong central transition, and the absence of low field transition with ΔM_s = 3 and 2 (the latter is reliably observed in cases where the secondary transitions in the spectrum (Fig. 2b) belong to the dimer).

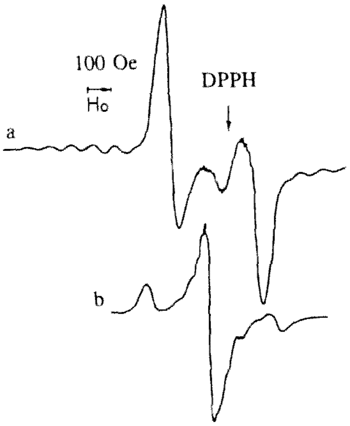

Fig. 2. EPR spectra of copper octa-tert-butyl-tetra-4,5-dibenzo-barrelenophthalocyanine at 77 K: a) in pentane; b) in dichloromethane.

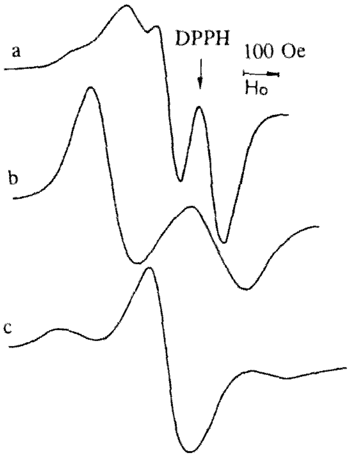

Fig. 3. EPR spectra of copper octa-tert-butyl-tetra-4,5-dibenzo-barrelenophthalocyanine at 300 K: a) in toluene; b) in pentane; c) in dichloromethane.

This spectrum can be assigned to a three exchangeable Cu^{2+} ion model with $S = 3/2$ [10]. The parameter value in this model is similar to that expected for systems of three molecules of substituted copper phthalocyanine placed on one axis mutually separated by a distance of 3.6 Å. Similar EPR spectra are also observed for solutions of copper etioporphyrin with low concentrations of Lewis acids [4].

The spectrum of I contained additional transitions for the dimer and stacking aggregates, thus the secondary transitions in the trimer were assigned to the dimer with a large D parameter value. Transitions at low fields with $\Delta M_s > 1$ could not be seen, evidently because of the low of D in the trimer.

In the powder, the ratio of monomer:dimer:trimer also depends on the rate of removal of solvent.

In liquid solutions at 300 K the spectra given in Fig. 3 are seen. Due to a large hydrodynamic radius, the movement of the investigated molecules is hindered and Brownian movement fails fully to average out the anisotropy in the spectrum. For this reason the lines are broadened, the position of the separate transitions being an average for the positions in the isotropic and anisotropic spectra. Nonetheless, it was possible to show that, depending on solvent, compound I occurred in liquid solution principally as monomers (Fig. 3a), dimers (Fig. 3b), and trimers (Fig. 3c) when the temperature was raised from 77 to 300 K.

It was also found that I tended to increase in aggregation along the series of solvents: toluene, chloroform, acetone, hexane, and dichloromethane in agreement with [8].

Evidently, the listed solvents interact differently with the investigated complex leading to a different orientation of the hydrocarbon substituents relative to the plane of the tetrapyrrole system. Moreover, in spite of steric hindrance, the molecules can approach to quite short distances (3.6 Å) at which an effective interaction can occur. Such short distances between phthalocyanine molecules containing bulky dibenzobarreleno fragments can only be realized in those cases where they are mutually turned through 45° about the common axis of symmetry. The aggregates formed are quite stable and are not dissociated at 300 K. Removal of solvent does not cause a significant change in the mutual positions of the molecules. There occurs only a shift in the equilibrium to one or the other form depending on the rate of removal. Some differences in the aggregate parameters for the powder or the frozen solution can be attributed to a weak perturbation in the solid state as a result of solvent removal.

Mechanical grinding of the powder causes a shift in the equilibrium towards the monomer complex.

EXPERIMENTAL

Copper octa-tert-butyl-tetra-4,5-dibenzobarrelenophthalo-cyanine (I) was obtained using [8].

EPR spectra were recorded on an RE 1307 radiospectrometer operating at a UHF frequency of 3 cm.

EPR experiments were carried out: a) in frozen solutions at 77 K; b) in liquid solutions at 300 K; c) as powders prepared by evaporation of solutions of I in the corresponding solvents. The following solvents were used: pentane, hexane, chloroform, toluene, acetone, and dichloromethane. The solution concentrations used were 10^{-2} to 10^{-3} molar.

The spectroscopic data are given in Table 1.

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