

## Copper Phthalocyanine

### Infrared Absorption Spectra of Polymorphic Modifications

BØRGE INGEMANN KNUDSEN

*The Research Laboratory, Kemisk Værk Køge A/S, Køge, Denmark*

Infrared absorption spectra of the  $\delta$ - and  $\varepsilon$ -modifications of copper phthalocyanine in the wavenumber range 400–4000  $\text{cm}^{-1}$  are described and compared with the corresponding spectra of the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -modifications. A key is proposed making it possible to distinguish between the 5 polymorphic modifications.

It is known that the infrared absorption spectra of the polymorphic modifications  $\alpha$  and  $\beta$  of the blue metal chelate copper phthalocyanine ( $\text{C}_{32}\text{H}_{16}\text{N}_8\text{Cu}$ ) exhibit characteristic differences making it possible to identify the two crystal structures.<sup>1-3</sup> A recent investigation<sup>4</sup> claims that the  $\gamma$ -modification of copper phthalocyanine shows the same infrared absorption spectrum as the  $\alpha$ -modification. The newer patent literature contains information on still two different modifications,  $\delta$  and  $\varepsilon$ .<sup>5,6</sup> Infrared absorption spectra of the  $\delta$ - and  $\varepsilon$ -modifications have, so far as we know, never been published nor compared with the spectra of the other polymorphic modifications. This is done in the present paper.

*Nomenclature.* We use the nomenclature suggested by von Susich<sup>7</sup> calling the metastable modification which results when adding a solution of copper phthalocyanine in 100 % sulfuric acid to water the  $\alpha$ -modification while the modification obtained when treating the  $\alpha$ -modification with boiling toluene for several hours is called  $\beta$ . In the literature a few authors have used the opposite nomenclature.

The  $\gamma$ -modification is determined by the X-ray diffraction pattern in the Eastes patent<sup>8</sup> while the  $\delta$ -modification is given in the Brand patent.<sup>5</sup> The  $\varepsilon$ -modification is determined by the X-ray diffraction pattern in our patent.<sup>6</sup> When filing the original application<sup>6</sup> the designation  $\delta$  was used but when the Brand patent<sup>5</sup> was published it became obvious that this application had been filed 6 months prior to the Knudsen application<sup>6</sup> hence an attempt was made to change the designation to  $\varepsilon$ . However, it has not been possible to have the original  $\delta$  altered to  $\varepsilon$  in all the countries where the invention has been patented. In the future the designation  $\varepsilon$  is used.

## EXPERIMENTAL

*$\alpha$ -Modification.* Copper phthalocyanine (20 g) is dissolved in sulphuric acid, 100 %, (400 g) at 50°C, and added to water (8 l) at 50°C while stirring vigorously. The copper phthalocyanine is filtered off, washed with water and dried at 110°C. An X-ray diffraction pattern shows that solely the  $\alpha$ -form is present. The size of the primary crystallites is mainly within the range of 0.01–0.03  $\mu$  (electron microscope).

*$\beta$ -Modification.* 5 g of the aforementioned  $\alpha$ -modification is dispersed in pure toluene (200 g) and refluxed for 5 h. After cooling the copper phthalocyanine is filtered off, washed with toluene and dried at 110°C for 24 h at atmospheric pressure. An X-ray diffraction pattern shows that only the  $\beta$ -form is present. Electron microscope investigation shows needle-shaped crystals 1–10  $\mu$  long.

*$\gamma$ -Modification.* Prepared according to example 17 in the Eastes patent<sup>4</sup> by mixing copper phthalocyanine (20 g) with sulfuric acid, 96.9 %, (322 g) while stirring 1 h at 50–55°C. After cooling to 2°C water is added while stirring to a sulphuric acid strength of 60 %; temperature is kept below 20°C. Stir 2 ½ h at 20–27°C and pour into water (8 l) at 10°C. Isolate the copper phthalocyanine by filtration, washing, reslurrying in water, heating to 95°C, filtration and drying at 110°C. An X-ray diffraction pattern agrees with the one published by Eastes. The length of the primary crystallites is mainly within the range of 0.3–1.0  $\mu$  (needles).

*$\delta$ -Modification.* Prepared according to example 1 in the Brand patent;<sup>5</sup> 25 parts of the copper phthalocyanine are dissolved in 250 parts of 98 % sulphuric acid and the solution is added during 30 min to a stirred emulsion of 440 parts of benzene in 800 parts of water containing 5 parts of Turkey Red Oil at 20°C. During the addition the temperature is allowed to rise from about 20°C to about 38°C. The emulsion separates into 2 layers and the precipitated phthalocyanine is in suspension in the benzene layer. The mixture is allowed to stand at room temperature for 48 h and the solid is then filtered off, washed with ethanol and finally with water until free of acid, and then dried at 70°C. An X-ray diffraction pattern shows the same characteristic lines as mentioned in the Brand patent for the  $\delta$ -modification. Particle size range 0.07–0.3  $\mu$ .

*$\epsilon$ -Modification.* Prepared as mentioned in the Knudsen patent<sup>6</sup> by grinding a mixture of sulphuric acid, 98 %, (295 g), copper phthalocyanine (400 g), sodium chloride (1500 g), and urea (350 g) for 18 h at 50–60°C. After this the grinding mixture is added while stirring to water (17 l) at 10°C over a period of 10 min. The water suspension is heated to 95°C and the phthalocyanine isolated by filtration, washing; drying at 70°C. An X-ray diffraction pattern is identical with the one published in the patent.<sup>6</sup> Particle size range 0.03–0.1  $\mu$ .

The instrument used for the experiments is a Perkin-Elmer double-beam infrared spectrophotometer, model 337, with a grating monochromator. The copper phthalocyanine is dispersed in an agate mortar in nujol (400–1330  $\text{cm}^{-1}$ ) or in hexachlorobutadiene (1330–4000  $\text{cm}^{-1}$ ), respectively, with 10 % phthalocyanine in the dispersion. KBr cells were used. All spectra were run at 25°C.

## RESULTS

Table 1 contains the wavenumbers for all the absorption lines in the spectra of the 5 polymorphic modifications of copper phthalocyanine in the range 400–4000  $\text{cm}^{-1}$  while Fig. 1 shows the spectra in the range 400–1330  $\text{cm}^{-1}$  only, partly because the instrument used gave 2 separate spectra of different accuracy, partly because no differences were found between the 5 spectra having few lines in the range 1330–4000  $\text{cm}^{-1}$ . The numbering of the absorption lines does not follow the one used by Sidorov *et al.*<sup>3</sup> because additional lines have been found within the wavenumber range investigated. The accuracy of the wavenumbers in the range 400–1330  $\text{cm}^{-1}$  is  $\pm 1.5 \text{ cm}^{-1}$  and in the range 1330–4000  $\text{cm}^{-1}$   $\pm 4 \text{ cm}^{-1}$ .

Table 1. Wavenumbers in  $\text{cm}^{-1}$  of infrared absorption lines of the 5 polymorphic modifications of copper phthalocyanine.

Line No.	$\gamma$	$\alpha$	$\beta$	$\delta$	$\varepsilon$
1	426	426			
2	434	434	434		
3				437	437
4	506	506	507	506	506
5	572	573	573	572	573
6	640w	640w	639	638	639
7			679w		679w
8	688w	689w	690	689	691
9	722	722			
10			730	729	729
11	754	754	755	755	755
12	769	769			
13			772	772w	
14	776w	776w			775
15	781		781	779	
16					785
17	801	802	800	800	801
18	863w	863			
19	869	870	870	871	869
20			876w	877	
21			879		879
22				882	
23	900	900	900	900	900
24	940w	940			
25	948	949	949		
26			956	955	958
27			982w		
28	1000	1002	1002	1001	1002
29	1068	1068	1068	1068	1068
30	1091	1091	1090		1092
31				1095	
32			1101		
33	1120	1120	1120	1119	1118
34			1164	1163	1161
35	1167	1167	1167w	1168	
36			1173		
37	1189	1189			1189w
38			1201w	1201w	
39	1287	1286	1287	1286	1286
40	1333	1332	1333	1332	1332
41	1420	1422	1420	1422	1420
42	1464	1466	1464	1464	1464
43	1480	1481w	1480w	1480w	1480w
44	1508	1509	1508	1508	1508
45	1592w	1590w	1590w	1589w	1588w

w = weak

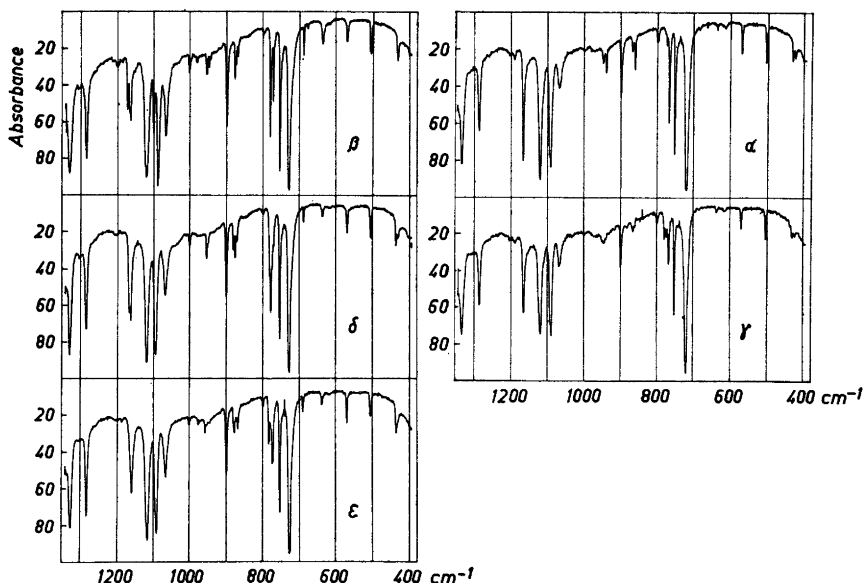


Fig. 1. Infrared absorption spectra of the 5 polymorphic modifications of copper phthalocyanine.

Absorption spectra were also run in the range 400–1330  $\text{cm}^{-1}$  on the 10 possible 2-component blends of the 5 polymorphic modifications the mixing ratio being 1:1, and on ( $\alpha + \epsilon$ )-blends in the ratios 4:1 and 1:4 and on a ( $\alpha + \beta$ )-blend in the ratio 4:1.

The absorption lines have been placed in Table 1 after a careful examination of spectra of the 5 basic modifications and spectra of the 2-component blends. The latter proved especially useful as a means of checking whether close lines do coincide or they actually differ (single resp. split lines). In the spectra from all 5 modifications there is some tendency to broadening of a few absorption lines which may hide double lines.

#### DISCUSSION

The absorption line wavenumbers found here for the  $\alpha$ - and  $\beta$ -modifications are in accordance with the results published by Ebert,<sup>1</sup> Kendall,<sup>2</sup> Sidorov *et al.*<sup>3</sup> and Assour.<sup>4</sup> The same is true for the  $\gamma$ -modification when comparing with Assour<sup>4</sup> except that we find a medium-strong line at 781  $\text{cm}^{-1}$  that Assour does not have and which is not present in the  $\alpha$ -spectrum. Repeated preparations of the  $\gamma$ -form using the procedure mentioned as well as using somewhat different conditions<sup>8,9</sup> have all given infrared spectra identical with the  $\gamma$ -spectrum published here. In all cases the  $\gamma$ -preparations used gave an X-ray diffraction pattern identical with the one published by Eastes differing from the X-ray pattern of the  $\alpha$ -modification. The shade of the  $\gamma$ -prepara-

tions has been considerably greener than that of the  $\alpha$ -preparations though all still blue. This means that the  $\alpha$ - and  $\gamma$ -modifications are not identical even if the infrared spectra show a great resemblance as do the X-ray diffraction patterns.

The X-ray diffraction pattern published by Assour for the  $\gamma$ -modification is different from the X-ray pattern for the  $\gamma$ -preparation we have used and also different from the pattern published by Eastes and by Honigman *et al.*<sup>10</sup> for the  $\alpha$ IIa-modification.  $\alpha$ II is used by Honigman *et al.* as a term for Eastes'  $\gamma$ -modification and "a" means that the X-ray pattern has sharp lines. The X-ray pattern published by Assour for the  $\gamma$ -form is identical with the pattern we have obtained from well-crystallized  $\alpha$ -preparations and with the pattern published by Honigman *et al.* for the  $\alpha$ Ia-modification, being a well-crystallized  $\alpha$ -preparation of unspecified particle size. When using the well-crystallized  $\alpha$ -preparation just mentioned (needles, 0.3–1  $\mu$  long) we get an infrared absorption spectrum identical with the one shown in Fig. 1. As far as we can see the  $\gamma$ -preparation used by Assour has been a well-crystallized  $\alpha$ -preparation. This explains Assour's results and conclusions regarding the  $\gamma$ -modification.

The infrared absorption spectra for the  $\delta$ - and  $\varepsilon$ -modifications differ as to several lines from each other and from the  $\beta$ -modification even if they both have some resemblance with the  $\beta$ -modification. If a very heavy mechanical treatment is used when dispersing copper phthalocyanine in nujol, especially at high pigment/nujol ratios, a change of modification may occur; *e.g.*, the  $\beta$ -modification shows an increasing content of  $\alpha/\gamma$ -form with increasing mechanical treatment.

Based on the results in Table 1 it is possible to set up several keys to be used in determining modifications in unknown copper phthalocyanine preparations. If only one or substantially one unknown modification is present the problem is a rather simple one. The key shown in Table 2 is preferred. Absorption lines are present in the  $\beta$ - and  $\delta$ -spectra at 779–781  $\text{cm}^{-1}$ . Because of this the  $\gamma$ -modification is identified through lines at both 722  $\text{cm}^{-1}$  and 781  $\text{cm}^{-1}$  while the  $\alpha$ -modification is identified by the line 722  $\text{cm}^{-1}$  being present and the line 781  $\text{cm}^{-1}$  being absent at the same time.

Table 2. Key for determining modifications in unknown copper phthalocyanine preparations.

1.	2.	Modification present
$\text{cm}^{-1}$	$\text{cm}^{-1}$	
722	781	$\gamma$
722	781 missing	$\alpha$
730	1173 and 1101	$\beta$
730	1095 and 1168	$\delta$
730	785 and 775	$\varepsilon$

The method of discerning the  $\beta$ -,  $\delta$ -, and  $\varepsilon$ -modifications is rather simple to use. In a blend of two modifications it is possible to identify the  $\beta$ -,  $\delta$ -, and/or  $\varepsilon$ -modifications. It is generally possible to distinguish between the  $\alpha$ - and  $\gamma$ -modifications if the  $\varepsilon$ -modification is present while you cannot make a safe distinction between those two when the  $\beta$ - or the  $\delta$ -modification is present. In a 2-component  $\alpha/\gamma$ -blend reasonable amounts of  $\gamma$  may further be detected. Thus it should be possible with the above key to identify 6 of the 10 possible 2-component blends if the components are present in reasonable amounts.

The experiments show that it is easy to distinguish 20 %  $\beta$ -modification in an  $\alpha/\beta$ -blend, 20 %  $\varepsilon$ -modification in an  $\alpha/\varepsilon$ -blend and 20 %  $\alpha$ -modification in an  $\alpha/\varepsilon$ -blend and that this is not the lower limit of the method. By comparing the relative intensities of the absorption lines in Table 2 it is possible to use the IR-method to determine the relative concentrations of modifications in 2-component-blends. The accuracy of the method depends upon the types of modification present in the blend. It is also important to use an IR-instrument of high accuracy.

The fact that it is possible through infrared absorption spectrophotometry to find differences between polymorphic modifications of the same chemical compound, copper phthalocyanine, is possibly due to changes in the forces between the molecules of the crystal going from one modification to another having an influence on the bond energies within the phthalocyanine molecule. It is obvious that the influences are greater at the outer edges of the phthalocyanine molecule, *i.e.* at the 4 benzene rings. It is known that *o*-disubstituted benzene rings may give IR-bands in the ranges 430–490  $\text{cm}^{-1}$  (C–C, out of plane bending), 735–775  $\text{cm}^{-1}$  (C–H, out of plane vibrations), 1000–1300  $\text{cm}^{-1}$  (C–H, in plane hydrogen bending), and 1470–1510  $\text{cm}^{-1}$  (C–C, ring stretching).

A considerable part of the strongest IR-absorption lines from the 5 modifications investigated here are located within the above 4 wavenumber ranges.

The differences in absorption wavenumbers between the modifications are mainly found within the ranges 720–790  $\text{cm}^{-1}$  and 1090–1180  $\text{cm}^{-1}$  as seen in Table 1, *i.e.* within the absorption ranges of the C–H bonds of the benzene molecule. The modification changes do not give rise to any shifts in the wavenumber range 1600–1700  $\text{cm}^{-1}$ , a range where C=N stretching bands in aromatic compounds often occur. Absorption lines corresponding to N–Cu-vibrations are to be found outside the wavenumber range investigated here (at lower wavenumbers).

Several absorption lines were found unchanged in all 5 modifications. This is the case with the lines at 755, 900, 1119, 1286, and 1332  $\text{cm}^{-1}$ .

When investigating compounds of very small particle size (0.01  $\mu$ –0.5  $\mu$ ) showing polymorphism it is often very difficult by the X-ray diffraction method to get sharp and high peaks on the patterns. No such difficulty is encountered when using the IR-method.

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