

Identification of Polymorphic Forms of Crystals by Infrared Spectroscopy

DAVID N. KENDALL

Calco Chemical Division, American Cyanamid Co., Bound Brook, N. J.

While studying the relation between the spectra and structure of pigments, it was found that infrared techniques can be conveniently and successfully applied to distinguish between different crystalline forms of substances of the same chemical composition. Infrared spectroscopy has been applied to the identification and determination of polymorphic forms of both organic and inorganic crystals. The method complements and supplements the x-ray, microscopical, and electron diffraction techniques. The advantages and disadvantages of these tech-

niques for study of polymorphism are discussed. The value of the infrared method is illustrated by results obtained on such pigments as the Para Reds and copper phthalocyanine blues. Results on the titanium dioxides illustrate the limitation of this infrared technique when applied to certain inorganic crystals. From application of the method knowledge can be obtained of how the molecular or molecular-ionic species are arranged and oriented in the crystal lattices of polymorphic substances by empirical interpretation of infrared absorption spectra.

THE use of x-ray (30), light microscopical (15), electron microscopical, and electron diffraction (7) techniques in the identification of polymorphic forms of crystals is known. It has now been discovered that infrared techniques can also be applied conveniently and successfully to distinguish between different crystalline forms of substances of the same chemical composition. This new infrared method can in certain cases detect smaller quantities of polymorphs than previously used techniques. It is rapid, employs small samples, and is not affected by the difficulties of crystal morphology characteristic of x-ray and microscopical methods. Permanent records in the form of infrared spectrograms are obtained which can be quickly referred to at any time in the future when the occasion demands.

The infrared spectroscopical technique described herein was developed primarily for analyzing polymorphic pigments and dyes, but the same procedures can be applied to other organic and inorganic crystals. The method involves obtaining the near infrared spectra of the pure polymorphs and then using these spectra to identify qualitatively and determine quantitatively the polymorphic forms that are present in any given sample of crystals.

Earlier workers have used infrared experimentally to show differences in the polymorphic forms of calcium carbonate (10, 16, 21), diamond (22, 26, 27, 29, 31), and quartz (23). On the theoretical side papers have been published on the selection rules for the Raman and infrared spectra of molecular (6) and ionic (3) crystals, on the general theory (2, 9, 11) of the vibrational spectra of crystals, and on the polarized infrared spectra (12) of inorganic salts.

To date, infrared spectroscopy has been used only to show differences between polymorphic forms of inorganic crystals. The present work extends the infrared techniques to the identification and determination of polymorphic forms of both organic and inorganic crystals.

The sharpest spectra of ground particles of a crystalline material will be obtained, as first pointed out by Pfund (18, 19), when the crystals under study are of a size less than the wave length of the infrared radiation, because of scattering. The spectra reported on herein were obtained on particles of diameters less than 5 microns, with the exception of the brookite spectrum.

The absorption curves illustrated in this paper are shown for the region from 5000 to 650 cm^{-1} . Spectral frequencies of the bands unique to each polymorph of a given crystal are shown under Results and Discussion. Absorption spectra are reported for polymorphs of the para toners, copper phthalocyanine blues,

and titanium dioxides. Interpretation of these spectra has been made by means of empirical correlations based on both published (1) and unpublished observations.

EXPERIMENTAL

All spectra reported were obtained with a Perkin-Elmer Model 12B infrared spectrometer. The instrument was calibrated using known absorption bands of water vapor, carbon dioxide, and ammonia.

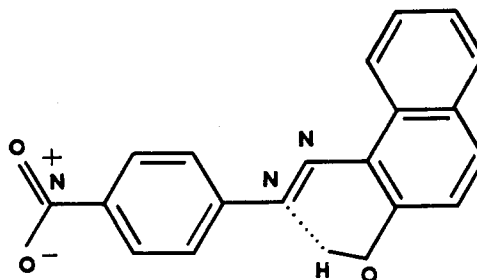


Figure 1. Proposed Structural Formula of Para Red

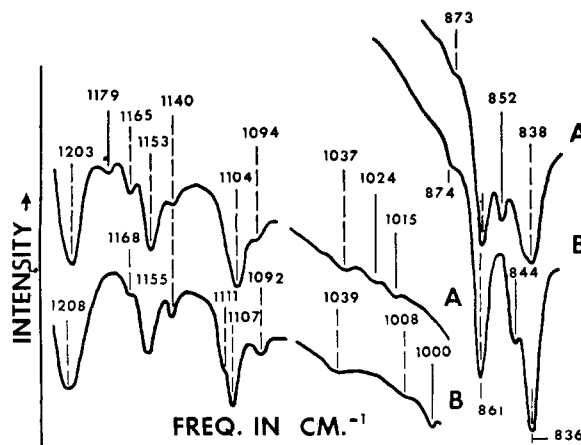


Figure 2. Polymorphism of Para Red

A. Blue shade
B. Yellow shade
Samples run as Nujol mulls

The crystalline powders were milled in Nujol or perfluorokerosene on a hard opal glass plate with a glass muller. Several mullings were made in the preparation of each sample, the number depending on the ease of dispersion. Usually two grindings were sufficient. With the exception of brookite, the particle diameters of all samples examined were less than 5 microns before the mulling process began. The milled sample was placed on a flat

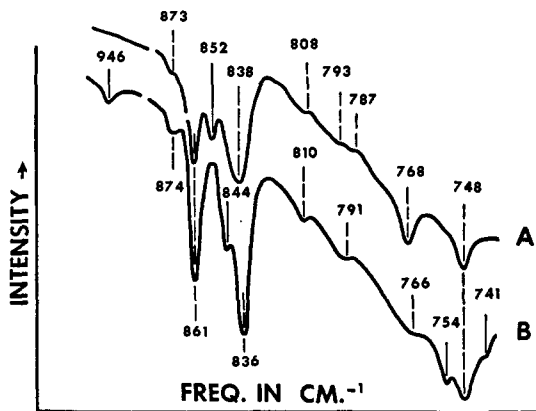


Figure 3. Polymorphism of Para Red

A. Blue shade
B. Yellow shade
Samples run as Nujol mulls

rock salt plate and spread out into a uniform film by applying manual pressure to another flat plate atop the sample. The plates and sample were then held in position in a simple cell comprising flat metal fore- and backplates held together by three threaded pins, two at one extremity, one at the other. Threaded knurled knobs allowed the maintenance of the proper amount of pressure. Visual observation of the sample through the plates quickly indicated whether a satisfactory dispersed film had been obtained.

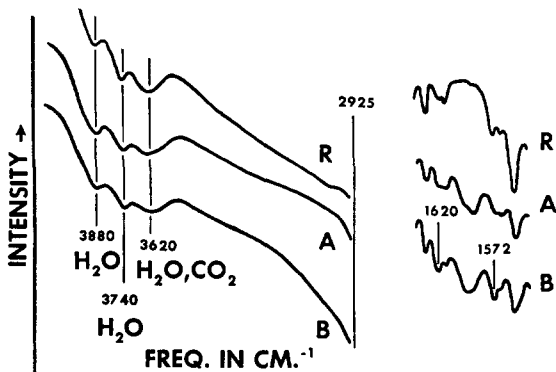


Figure 4. Polymorphism of Para Red

A. Blue shade
B. Yellow shade
R. Radiation
Samples run as Nujol mulls

Infrared absorption spectra were then run and the resulting spectra measured and interpreted. Over each of eight segments of the spectrum covering the range from 5000 to 650 cm^{-1} a constant slit width was employed, and these slit widths were the same for every spectrum. Philpotts *et al.* (20) have emphasized recently the importance of constant slit width to infrared spectroscopical investigations.

RESULTS AND DISCUSSION

Figures 1 to 19 show the infrared absorption spectra of polymorphic forms of Para Red, copper phthalocyanine blue, and titanium dioxide as well as the structural formulas of these substances. The graphs show intensity versus frequency in recip-

rocal centimeters. The energy of the source is, of course, superimposed upon the radiation transmitted by the sample in each spectrum. While complete spectra from 5000 to 650 cm^{-1} were obtained for each substance, as will be observed in some plots, only segments of such spectra are shown for reasons of space conservation. Breaks in the spectral curves in certain figures indicate that less significant regions of the spectrum have been omitted. On the "intensity" ordinate, spectrograms have been arbitrarily displaced vertically in order to present comparisons of polymorph spectra over the same spectral intervals. The dashed and full frequency verticals were for the purpose of oral presentation of this paper. In general, the full lines represent the absorption frequencies where the differences between two given polymorphic forms are most readily observed. Most samples were run in the solid state dispersed in Nujol or perfluorokerosene. Several solution spectra are presented, however, for reasons given later.

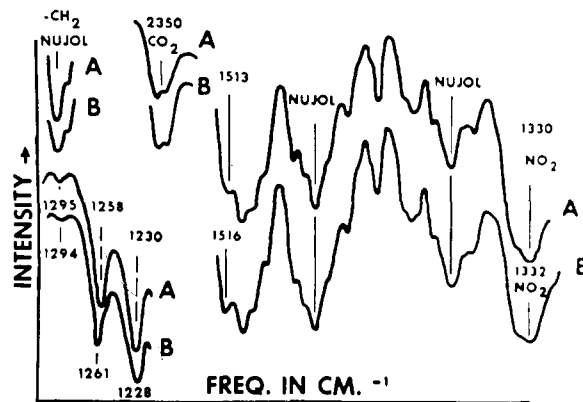


Figure 5. Polymorphism of Para Red

A. Blue shade
B. Yellow shade
Samples run as Nujol mulls

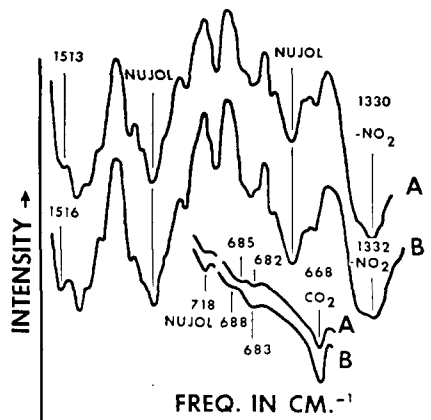


Figure 6. Polymorphism of Para Red

A. Blue shade
B. Yellow shade
Samples run as Nujol mulls

Para Reds. Figure 1 shows the structural formula of Para Red proposed on the basis of its chemical constitution and properties, but most particularly on the basis of the present infrared study. Para Red pigment is prepared (33) from diazotized *p*-nitroaniline, which yields when treated with sodium hydroxide a stable isodiazotate, $\text{O}_2\text{NC}_6\text{H}_4\text{N}_2\text{ONa}$. Upon acidification with hydrochloric acid and coupling with 2-naphthol, Para Red results.

Control of the appropriate variables in the process gives rise to the blue shade or the yellow shade of the pigment. The coupling in either case takes place in the 1-position.

Figures 2 through 6 show the infrared absorption spectra of the blue and yellow shades of Para Red as Nujol mulls. The spectral regions of greatest interest in the 5000 to 650 cm^{-1} range are presented. Inspection of the figures mentioned reveals that the blue shade and the yellow shade of Para Red have different solid state absorption spectra. The blue shade crystals show bands at 1179, 1024, 1015, and 852 cm^{-1} which the yellow shade crystals lack. The latter absorb at 1620, 1572, 1000, 946, 844, 754, and 741 cm^{-1} while the blue shade crystals do not.

Figures 7 and 8 present several segments from the spectra of the blue and yellow shades of Para Red in 0.5% by weight chloroform solution together with the corresponding spectral regions of chloroform itself for comparison. It is evident that a sufficient concentration of each shade of Para Red dissolves in chloroform to make a valid comparison of their spectra. The presence of the 845- cm^{-1} band—e.g., in the spectra of the blue and yellow shades (curves B and C, Figure 8)—and its absence in the chloroform spectrum (curve A) prove that the Para Reds have dissolved in chloroform in sufficient concentration to reveal their presence in their absorption spectra. Several other bands characteristic of the Para Reds will be observed in the 1075 to 1250 cm^{-1} region of curves B and C in Figure 8. The absence of these bands in curve A, the chloroform spectrum, will be noted. The complete rock salt spectrum of the blue shade in chloroform solution is identical to that of the yellow shade in the same solvent. This experimental evidence proves the two shades are identical in chemical composition. The fact that the infrared absorption spectrum of the blue shade is different from that of the yellow shade in the solid state shows the two shades to be polymorphic forms.

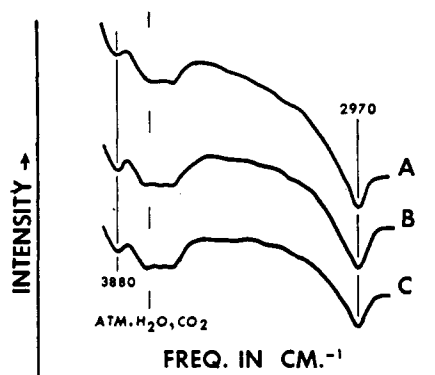


Figure 7. Polymorphism of Para Red

A. Chloroform
B. Blue shade
C. Yellow shade
B and C in chloroform solution

Polymorphism is particularly common in the case of organic dyes and pigments, as first shown by extensive x-ray powder diffraction studies begun about 1933 in Germany (30). Polymorphism of organic pigments has also been observed by electron microscopy and electron diffraction (?).

The experimental evidence cited above for the two shades of Para Red shows that substances of the same chemical composition which have their molecules or molecular species oriented differently spatially to form crystals of different space lattices can be readily identified and distinguished from each other by means of their different infrared spectra. This finding applies also to crystals made up structurally of ions, as was first reported

by Nyswander (16) in his work on calcite and aragonite. The infrared technique also is applicable to those crystals in which ionic, covalent, van der Waals, and other types of chemical binding are all involved in the spatial arrangements of the ions and molecules in the unit cell and the crystal lattice.

Figure 4 shows that no free or bonded hydroxyl absorptions are found in the spectrum of either the blue or yellow shade Para Red crystals. Figure 7 gives the absorption spectra of the blue shade (curve B) and yellow shade (curve C) of Para Red in chloroform solution in the high frequency —NH— and —OH region together with the spectrum of chloroform (curve A) in the same region. Here also, no free or bonded hydroxyl bands are found for either shade. It is, therefore, likely that extremely strong hydrogen bonding exists between the hydroxyl hydrogen and the diazo nitrogen nearest the nitro-substituted benzene ring in both shades of Para Red in the crystalline state as well as in solution in chloroform. This spectroscopical finding is compatible with the known virtual alkali insolubility of the Para Reds. That the N...H—O bonding is to the diazo nitrogen nearest the nitro-substituted benzene ring is very certain on the grounds of ring strain, bond distances, and steric considerations (17).

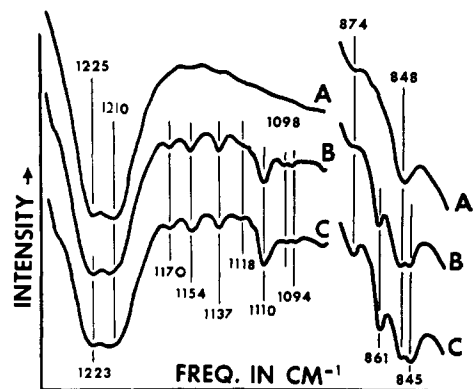


Figure 8. Polymorphism of Para Red

A. Chloroform
B. Blue shade
C. Yellow shade
B and C in chloroform solution

The possibility of a very weak band at 3030 cm^{-1} was noted in a perfluorokerosene mull spectrum of Para Red blue shade. The presence or absence of such a band was ambiguous, however, and the spectra of the Para Reds should be reinvestigated in the —NH— and —OH region with the higher dispersion afforded by lithium fluoride. This 3030- cm^{-1} absorption, however, if it does exist, would appear to be of too low frequency for a bonded —OH. It is probably an aromatic C—H stretching frequency. For the Para Reds in the solid state or in solution, a bonded hydroxyl absorption is entirely missing, or owing to the great strength of the hydrogen bonding it is shifted into and obscured by C—H absorptions. The absence of both free and bonded —OH absorptions in a substance containing an —OH grouping is unusual but not unknown. Its absence was observed by the author in these laboratories in 1946 in the Nujol mull spectrum of 1-hydroxyanthraquinone (5, 14). Here also the reason for the absence of any hydroxyl absorption was found to be the presence of extremely strong hydrogen bonding, which in this case, was an O...H—O bond.

The possibility of a ketonic grouping with the hydroxyl hydrogen shifting to the nitrogen in the molecular structure of Para Red both as it exists in solution or in either of its dimorphic forms is ruled out by the absence of any ketonic carbonyl or —NH— absorptions in any of the Para Red spectra. The ketonic

carbonyl absence is evident from examination of Figure 9, which shows the C=O stretching region for the blue shade (A) and the yellow shade (B). For ready comparison, the radiation curve for the same region is shown as curve R. The 1620-cm.⁻¹ band observed in the yellow shade spectrum is too strong for a para substituted phenyl ring absorption and is believed to represent a type of quasi-carbonyl absorption. When the hydrogen of a ϕ -OH is strongly bonded to a diazo nitrogen linked to the same aromatic ring, the carbon-oxygen bond acquires considerable

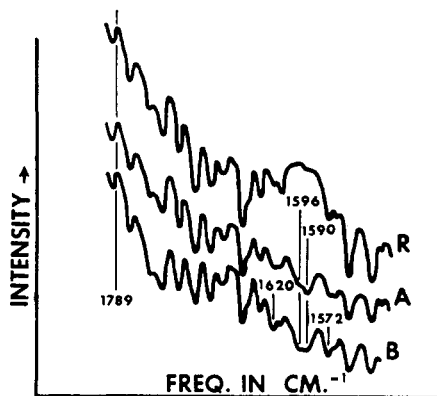


Figure 9. Polymorphism of Para Red

A. Blue shade
B. Yellow shade
R. Radiation
Samples run as Nujol mulls

double bond character. In the present case, the 1620-cm.⁻¹ absorption of this hybrid carbon-oxygen is below the normal frequency of about 1680 cm.⁻¹ for a true carbonyl, yet well above the normal 1235-cm.⁻¹ absorption for a true single bond C—O of a ϕ -OH. The packing of the Para Red molecules in the blue shade crystal is such as not to allow the occurrence of this 1620-cm.⁻¹ absorption observed in the yellow shade. The —NH— absorption absence is evident from inspection of Figure 4.

The structural formula proposed for Para Red given in Figure 1 is based on the spectroscopical evidence and reasoning given above. Considerations of bond angles and distances (17) show that the Para Reds are trans isomers with respect to the azo linkage.

While Figures 2 through 4 point out the infrared spectral differences between the blue and yellow shades of Para Red, Figures 5 and 6 emphasize the spectral similarities observed when two polymorphs are examined in the infrared. These similarities are to be expected, since the two forms are but different spatial expressions of the same chemical composition. In general, polymorphic forms of organic crystals with their preponderance of nonpolar intermolecular linkages will give rise to a greater number of infrared spectral differences than inorganic crystals with their preponderance of ionic linkages.

Evidence that the infrared spectral differences between crystals of the blue and yellow shades of Para Red were no accident of chance is shown by the fact that three samples of this pigment of shade unknown to the author were successfully identified from their infrared spectra as to polymorphic form.

From empirical correlations of the data in Figures 2 through 6 based on published material (1) and studies in these laboratories, it is probable that the molecules in the crystals of Para Red yellow shade are oriented in such a way as to give the 2-naphthalene ring more freedom to vibrate than in the Para Red blue shade crystals. In the blue shade crystal, on the other hand, the benzene ring containing the hydroxyl grouping has more freedom to vibrate than in the yellow shade crystal. The yellow shade crystals were found to give more infrared absorption bands,

33, than the blue shade crystals, which gave 31 absorptions. This probably means that the yellow shade has a lesser degree of crystalline order, more types of intermolecular linkages, and hence more absorption bands. The blue shade is then probably the thermodynamically stable one, that is at room temperature.

Frequencies of the absorption bands for the two polymorphic forms of Para Red as Nujol mulls in the rock salt region are given in Table I.

Table I. Nujol Mull Spectra of Blue and Yellow Shade Para Reds in the Rock Salt Region

(Frequency in cm. ⁻¹)							
Blue Shade				Yellow Shade			
1596 m	1179 w	1015 w	808 w	1620 m	1168 w	1000 w	836 s
1590 m	1165 w	985 w	793 vw	1572 m	1155 m	984 m	810 w
1513 m	1153 m	981 m	787 vw	1516 s	1140 m	978 w	791 w
1330 s	1140 w	963 w	768 m	1332 s	1111 m	961 vw	766 w
1295 w	1104 s	873 w	748 m	1294 w	1107 s	946 m	754 m
1258 m	1094 w	862 m	685 w	1261 m	1092 m	874 w	748 m
1230 m	1037 w	852 m	682 w	1228 m	1039 w	861 s	741 w
1203 s	1024 w	838 s		1208 s	1008 w	844 m	688 w
							683 w

m, medium; s, strong; w, weak.

A band is classified as weak if its absorbance is less than 10% of the absorbance of the strongest band, as medium if between 10 and 60%, and as strong if greater than 60%.

Copper Phthalocyanines. Figure 10 shows the structural formula of copper phthalocyanine. Linstead *et al.* (4) found the phthalocyanine molecule is composed of four isoindole units joined together by four extracyclic nitrogens to form a compound having a strainless 16-membered central ring with one metal atom in the center in the case of the metallic derivatives of phthalocyanine.

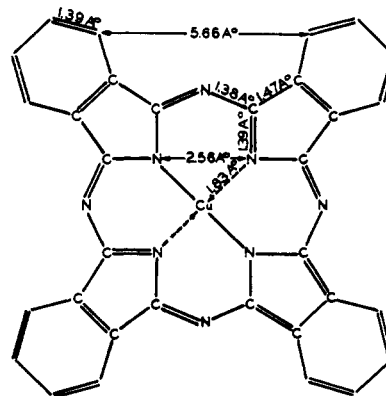


Figure 10. Structural Formula of Copper Phthalocyanine

Robertson (23, 24) and Robertson and Woodward (25) in careful studies investigated the complete crystal structure of phthalocyanine and its metallic derivatives. Their results confirmed the earlier work (4), yielded bond lengths, and showed the metal atom to be located in the center of the molecule and that it did not alter substantially the form of the phthalocyanine portion. The structure of copper phthalocyanine must be regarded as one continuous conjugated system. Robertson had only one form of copper phthalocyanine available to him—namely, the alpha form. This was prepared by sublimation as large needle crystals totally unsuited for pigment use but of definite value for x-ray diffraction study. He reported no data on any other form. Susich (30) showed by x-ray diffraction that copper phthalocyanine exists in two different crystal forms. Here the Robertson form is called "alpha," because historically this crystal form was the first to be identified, and the first commercial pigment form is called "beta."

Figures 11 through 14 show the infrared absorption spectra of two polymorphic forms of copper phthalocyanine. The spectra from 4000 to 650 cm^{-1} are presented for the alpha form, curve A, and the beta form, curve B, as Nujol mulls. Inspection of these figures reveals that the alpha and beta forms of copper phthalocyanine yield different spectra which are readily distinguishable one from the other. Here again the techniques of infrared spectroscopy enable one to identify and distinguish between polymorphic forms of organic crystals.

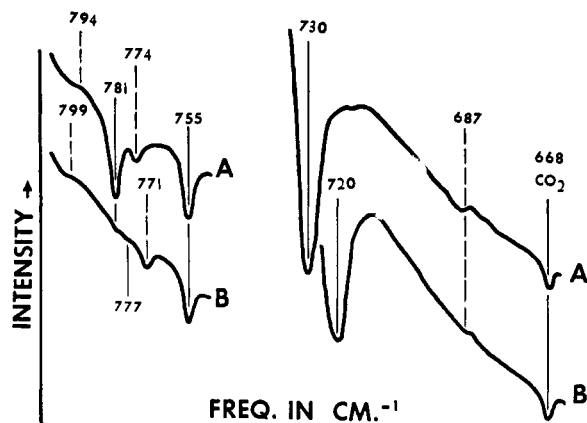


Figure 11. Polymorphism of Copper Phthalocyanines

A. Alpha form
B. Beta form
Samples run as Nujol mulls

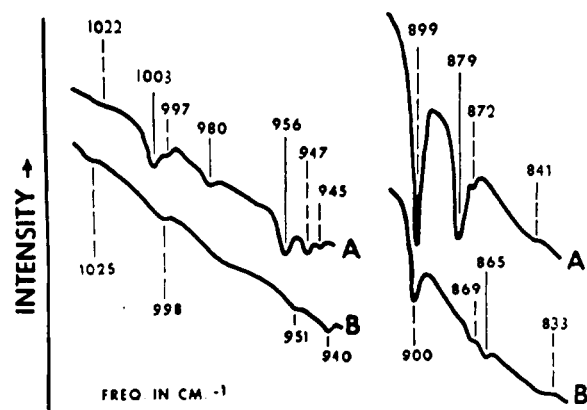


Figure 12. Polymorphism of Copper Phthalocyanines

A. Alpha form
B. Beta form
Samples run as Nujol mulls

The alpha form, spectrum A, has 10 bands not found in the spectrum of the beta form. These are the 730-, 879-, 956-, 980-, 1003-, 1101-, 1173-, 1606-, 3152-, and 3210- cm^{-1} bands. The beta form, spectrum B, has three bands not observed in the spectrum of the alpha form. These are the 720-, 865-, and 3115- cm^{-1} absorptions. The most striking infrared spectral difference between the two polymorphic forms is the strong 730- cm^{-1} band in the alpha form as opposed to the also strong 720- cm^{-1} band in the beta form (as seen in Figure 11). The other readily observable differences will be found upon inspection of Figures 11 through 14.

The difference between the crystal structure of the alpha and a suggested structure for the beta form (32) when a projection is taken parallel to the crystal plane of the respective polymorphic forms is shown in Figure 15. The two crystal forms differ only in the arrangement of the copper phthalocyanine molecules

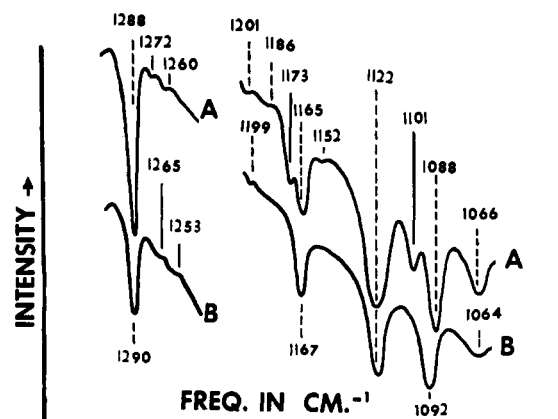


Figure 13. Polymorphism of Copper Phthalocyanines

A. Alpha form
B. Beta form
Samples run as Nujol mulls

within their respective crystal planes. The molecules in the alpha form present a "regular" array, those in the beta form a "staggered" array.

Because the rock salt infrared spectra of the two forms are different, the spectral differences must arise from the different effects that the intermolecular forces present in one form have on the intramolecular forces of that form as compared with the interaction of similar forces in the other form. That the effect of intermolecular forces on intramolecular forces will be different in the alpha and beta forms of copper phthalocyanine is evident upon examination of Figure 15.

Empirical interpretation of the spectral differences between the two forms reveals that probably the ortho disubstituted benzene rings and the C—N groupings are freer to vibrate in the alpha form of copper phthalocyanine than in the beta, while the C—H groupings are freer to vibrate in the beta form than in the alpha form.

Infrared spectra in the rock salt region were run on copper phthalocyanines crystallized in xylene and in aniline. Each of these spectra showed a strong 730- cm^{-1} band characteristic of the alpha form and also a weak 720- cm^{-1} band characteristic of the beta form. It, therefore, became of interest to work out a quantitative method of analysis for the determination of alpha and beta form copper phthalocyanines in mixtures of the two forms.

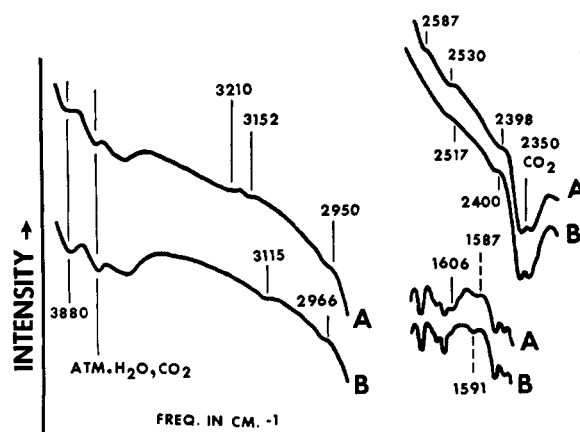


Figure 14. Polymorphism of Copper Phthalocyanines

A. Alpha form
B. Beta form
Samples run as Nujol mulls

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