TABLE III

VAPOR PRESSURE OF 1-PENTANETHIOL

Boiling point, °C. Water	Boiling point, °C. 1-Pentanethiol	Vapor pressure mm.	$p_{obsd} - p_{calcd}$ Eq. 1	$p_{obsd} - p_{calcd}$ Eq. 2
60.000	76.470	149.41	−0.01	−0.01
65	82.569	187.57	.00	+ .01
70	88.721	233.72	− .01	+ .01
75	94.918	289.13	+ .01	+ .02
80	101.167	355.22	− .01	− .01
85	107.457	433.56	+ .06	+ .06
90	113.802	525.86	+ .05	+ .02
95	120.193	633.99	+ .06	+ .05
100	126.638	760.00	− .01	− .03
105	133.131	906.06	− .11	− .09
110	139.671	1074.6	− .1	.0
115	146.255	1268.0	− .1	+ .1
120	152.896	1489.1	− .2	.0
125	159.580	1740.8	.0	+ .2
130	166.314	2026.0	+ .3	+ .3

The Entropy in the Liquid and Ideal Gas States.—The calorimetric and vapor pressure data have been used to calculate the entropy of 1-pentanethiol in the liquid and ideal gas states at 298.16°K. Table IV summarizes the results.

TABLE IV

1-PENTANETHIOL MOLAL ENTROPY, CAL. DEG.$^{-1}$

0–12°K.	Debye, 6° freedom, θ = 134.9	0.218
12–197.46°	Solid, graphical $\int C_{\text{satd}}\, d \ln T$	33.863
197.46°	Fusion, 4190/197.46	21.219
197.46–298.16°	Liquid, graphical $\int C_{\text{satd}}\, d \ln T$	18.882
Entropy (±0.15) of liquid at 298.16°K.		74.18
Vaporization, 9825/298.16		32.95
Compression, $R \ln p/760$		− 7.95
Gas imperfection		0.00
Entropy (±0.35) of ideal gas at 1 atm. and 298.16°K.		99.18

Discussion

The stated purpose of this investigation is to provide data that will guide the computations by incremental methods of the thermodynamic functions $S°$, $(H°_T - H°_0)$, $(H°_0 - F°_T)/T$ and $C°_p$ for the *n*-alkane thiols of interest. Reliable computation of such functions is not yet possible on the basis of existing data. However, it is of interest to compare the difference between ideal gas entropies for ethanethiol[2] and 1-pentanethiol with that between propane and *n*-hexane, which differ from the two thiols by the replacement of an SH group by a CH_3 group. The experimental ideal gas entropies at 298.16°K. for ethanethiol[2] and 1-pentanethiol (this paper) are 70.77 and 99.18 cal. deg.$^{-1}$ mole^{-1}, respectively. The corresponding values for propane[7] and *n*-hexane[8] are 64.51 and 92.93 cal. deg.$^{-1}$ mole^{-1}. The differences between the respective pairs are 28.41 and 28.42 cal. deg.$^{-1}$ mole^{-1}. This excellent agreement is undoubtedly partly fortuitous but suggests that similar incremental relationships exist between thiols as in hydrocarbons of related structure. Because of the extensive thermodynamic information already available for hydrocarbons, this circumstance will facilitate the compilation of tables of thermodynamic functions for the alkanethiols.

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(7) (a) K. S. Pitzer, *Ind. Eng. Chem.*, **36**, 829 (1944); (b) Kemp and Egan, THIS JOURNAL, **60**, 1521 (1938).

(8) Liquid entropy 298.16°K. = 70.76 cal. deg.$^{-1}$ mole^{-1}, D. R. Douslin and H. M. Huffman, *ibid.*, **68**, 1704 (1946); entropy of vaporization 298.16°K. = 25.29 cal. deg.$^{-1}$ mole^{-1}, from data of N. S. Osborne and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **39**, 453 (1947); compression, $R \ln (p/760) = -3.21$ cal. deg.$^{-1}$ mole^{-1}; gas imperfection, $(\partial B/\partial T)_P = 0.09$ cal. deg.$^{-1}$ mole^{-1}, B (defined by $PV = RT + BP$) $= -455 - 28.5 \exp 1175/T$ cc. mole^{-1}, previously unpublished but based on $(\partial C_p/\partial p)_T$ and ΔH_{vap} data of G. Waddington and D. R. Douslin, THIS JOURNAL, **69**, 2275 (1947).

BARTLESVILLE, OKLAHOMA

[CONTRIBUTION NO. 112 FROM JACKSON LABORATORY, E. I. DU PONT DE NEMOURS AND CO.]

Infrared Spectra of Organic Compounds Exhibiting Polymorphism

BY A. A. EBERT, JR., AND H. B. GOTTLIEB

RECEIVED OCTOBER 3, 1951

It has been shown that infrared spectrometry is a new and useful tool for the study of polymorphism. Examples of its use have been cited, including a series of five phthalocyanines and three other crystalline organic compounds. The polymorphic forms of the latter, while giving identical spectra in solution, showed as crystals marked differences in infrared absorption.

Little has been published about infrared absorption by polymorphic modifications of the same compound. If infrared spectra of a compound's crystal modifications were found to be identical, one could confidently conclude that transition from one form to the other does not involve intramolecular changes. If, on the other hand, the spectra of polymorphic crystal modifications were found to be not the same, one could not entirely dismiss the possibility of a transition, accompanied by intramolecular shifts of linkages in the latticed molecules. Dissimilarity of vibrations in crystal modifications of the same compound could be caused by mere difference in latticing, but it could also be due to a combination of two causes, different latticing together with different linkages inside the latticed molecules.

Actually, we discovered appreciable differences between infrared absorption spectra of diverse crystal modifications of the same compound. Indeed, the spectra could be thought to be those of separate compounds. This was the case with phthalocyanines, 2-chloro-4-nitrobenzoic acid, allylthiourea and anthranilic acid. Hence, it is difficult to identify a compound in its crystalline phase by reference to known spectra, if the latter do not include the spectra of all polymorphic forms of the compound.

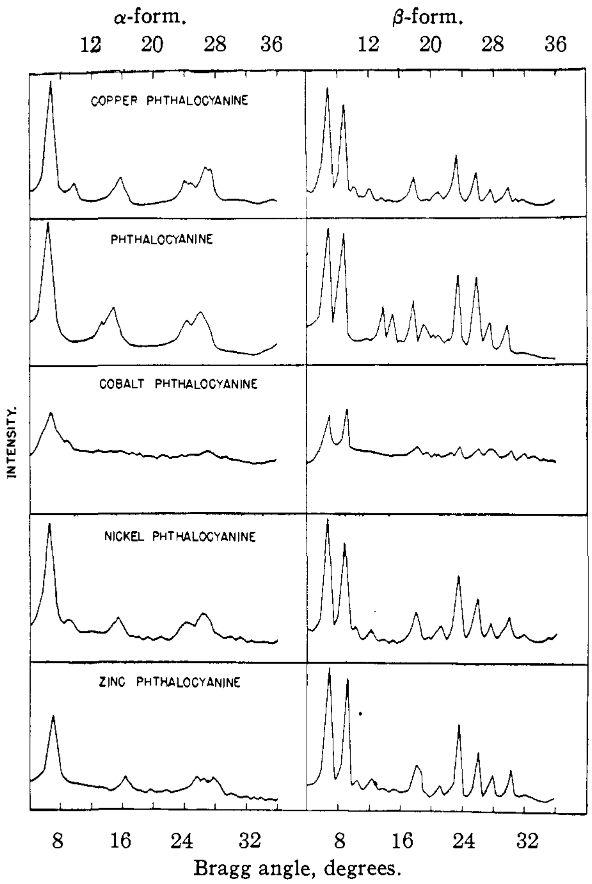

Fig. 1.—X-Ray diffraction patterns characteristic of the α- and β-forms of phthalocyanine and its derivatives.

Literature.—Well known are the changes in infrared absorption which are caused by changes of state (*e.g.*, Richards and Thompson[1]), but few publications refer to variations in infrared absorption which are the result of a compound's transition from one solid modification to another solid modification. Most of these publications have been concerned with detecting infrared absorption changes resulting from modification of the crystal form of inorganic compounds and one paper refers to crystallization in a polymer. However, the infrared spectral differences associated with the polymorphic modifications of crystalline organic compounds do not appear to have been previously investigated. Hunt, Wisherd and Bonham,[2] Keller and Halford,[3] and Wagner and Hornig[4] have reported that differences exist between infrared spectra of inorganic polymorphic forms. Mochel and Hall[5] have observed that new or more intense bands occur in crystallized neoprene which are absent in the amorphous polymer.

Lecomte[6] has described the effect of water of crystallization together with other studies on infrared spectra of inorganic crystals.

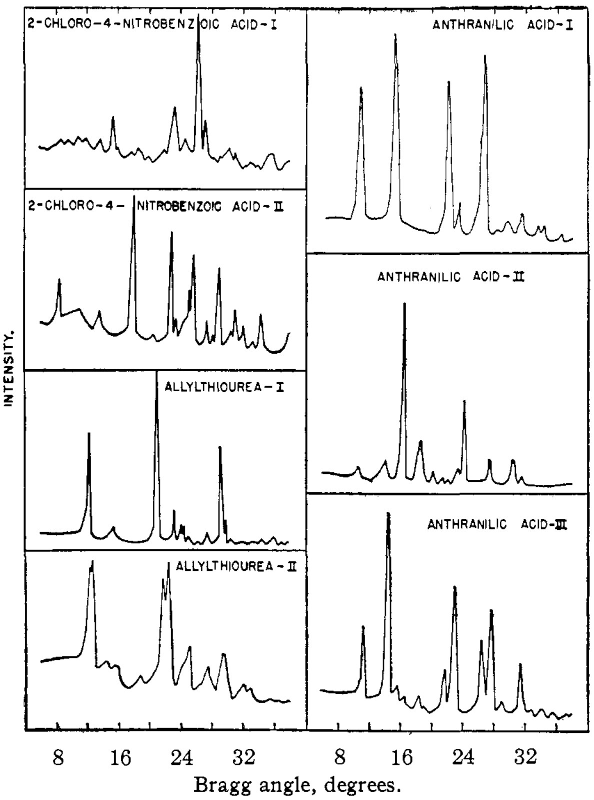

Fig. 2.—X-Ray diffraction patterns of the polymorphic forms of three crystalline organic compounds.

Barnes, Gore, Williams, Linsley and Petersen[7] and also Gore and Petersen[8] have shown the importance of considering crystal orientation effects in infrared spectroscopy because of the small inherent polarization of radiation in a prism spectrometer. Study of our X-ray diffraction patterns indicate that the materials included in our survey exhibit no strong orientation effects.

Information obtained in Germany after the war contained two references to polymorphism of metal phthalocyanines and its discovery by the X-ray method.[9,10] For this discovery, the American investigators gave credit to George Susich, who also discovered the polymorphism of metal-free phthalocyanine.[11] We have adopted Susich's nomenclature[12] calling "alpha," in all cases, the phthalocyanine modification which is unstable to transition in aromatic solvents, and "beta" the modification which is stable to transition when stored in aromatic solvents at room temperature. The patent literature mentions polymorphic pairs of copper,

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(1) R. E. Richards and H. W. Thompson, *Proc. Roy. Soc.* (*London*), **A195**, 1 (1948).

(2) J. M. Hunt, M. P. Wisherd and L. C. Bonham, *Anal. Chem.*, **22**, 1478 (1950).

(3) W. E. Keller and R. S. Halford, *J. Chem. Phys.*, **17**, 26 (1949).

(4) E. L. Wagner and D. F. Hornig, *ibid.*, **18**, 296 (1950).

(5) W. E. Mochel and M. B. Hall, THIS JOURNAL, **71**, 4082 (1949).

(6) Jean Lecomte, "Le Rayonnement Infrarouge," Gauthier-Villars, Paris, 1949.

(7) R. B. Barnes, R. C. Gore, E. F. Williams, S. G. Linsley and E. M. Petersen, *Anal. Chem.*, **19**, 620 (1947).

(8) R. C. Gore and E. M. Petersen, *Ann. N. Y. Acad. Sci.*, **51**, 924 (1949).

(9) U. S. Office of Technical Services, Publication Board Report 74892 (1947), pp. 9060-61. Obtained information of work by Kircher and Berthold.

(10) Field Information Agency Technical German Dyestuffs and Intermediates, FIAT Final Report 1313, Vol. III. Dyestuff Research, Technical Industrial Intelligence Division, U. S. Department of Commerce, Washington, D. C., 1948. Publication Board Report 85172. Obtained information of work by G. Susich, pp. 412 and 462.

(11) George Susich, *Anal. Chem.*, **22**, 426 (1950).

(12) R. H. Kienle[13] reversed this nomenclature. He calls Susich's alpha form "beta" and Susich's beta form "alpha."

(13) R. H. Kienle, Official Digest, Federation of Paint and Varnish Production Clubs, January, 1950, p. 48.

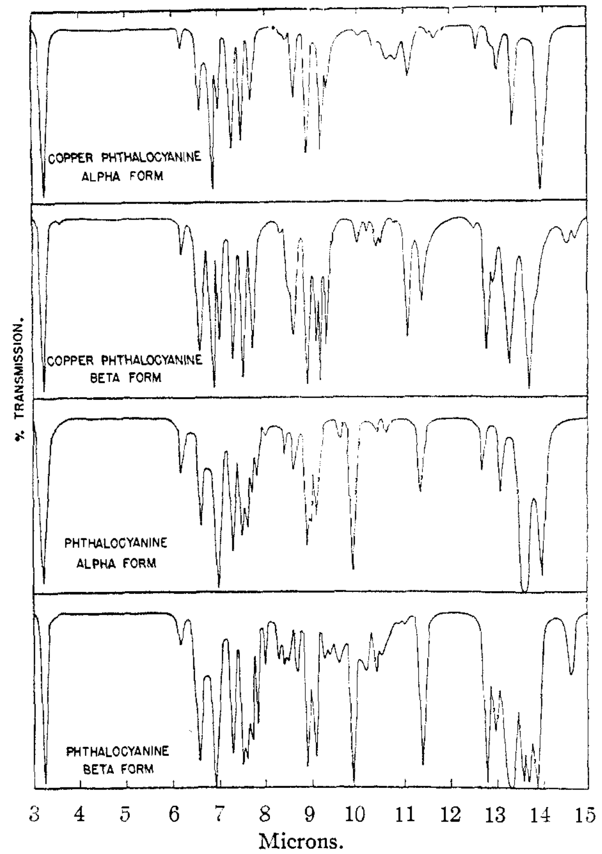

Fig. 3.—Infrared spectra of the alpha and beta forms of copper phthalocyanine and phthalocyanine in Nujol suspensions.

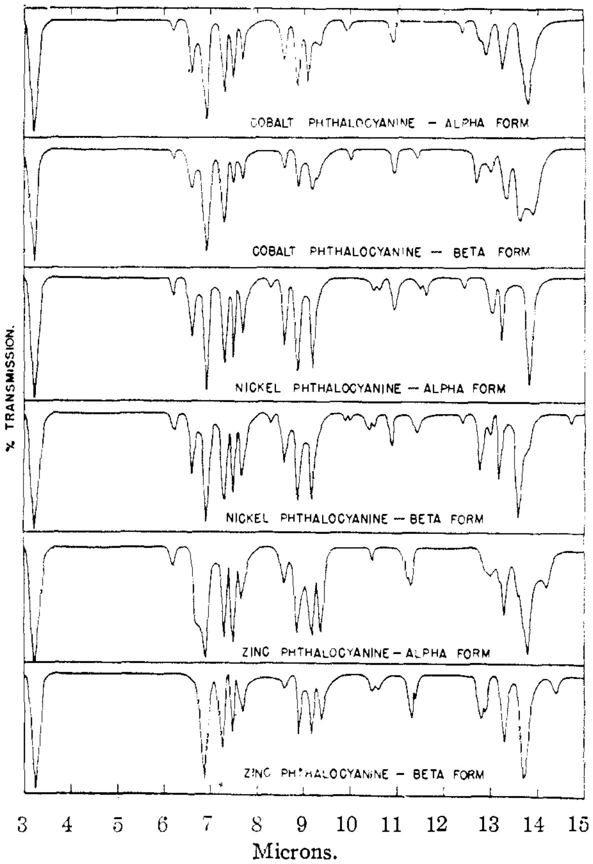

Fig. 4.—Infrared spectra of the α- and β-forms of three phthalocyanines in Nujol suspensions.

nickel and zinc phthalocyanines.[14] α- and β-copper phthalocyanine have also been found to give two characteristically different electron diffraction patterns.[15] The polymorphic modifications of allylthiourea and anthranilic acid have been described by W. C. McCrone.[16]

When this paper had just been completed, our attention was called to David N. Kendall's lecture on infrared spectra of polymorphic forms, given at the A.C.S. Meeting in Boston, Mass., April, 1951.[17]

Experimental

Sample Preparation. α-Copper Phthalocyanine.—A mixture of 82 g. of phthalonitrile with 10.6 g. of copper bronze was agitated in 400 ml. of ethyleneglycol at 137–140° for 24 hours. After cooling to 80°, the reaction mass was drowned into ethyl alcohol, isolated by filtration and then extracted with ethyl alcohol to remove all unreacted phthalonitrile. The alcohol was displaced by water and the aqueous presscake slurried in 1.5 l. of water containing 10 ml. of concentrated aqueous ammonia and 0.5 g. of ammonium chloride for 1.5 hours at 70°. After filtration, this purification step was repeated. The yield of the dried α-copper phthalocyanine was 77%. Found: Cu, 11.37; N, 19.13. Calcd. for $C_{32}H_{16}N_8Cu$: Cu, 11.04; N, 19.48. The copper phthalocyanine separated from the ethyleneglycol in the modification which is unstable in aromatic solvents.

β-Copper Phthalocyanine.—A mixture of 155 g. of phthalonitrile, 315 ml. of nitrobenzene, 49.6 g. of anhydrous copper sulfate and 13 g. of ammonium sulfate was heated to 105° and a stream of gaseous ammonia was passed through the suspension until ammonia was no longer absorbed. Then, the flow of ammonia was reduced to a slow current. The reaction mass was heated to 225 to 230° over 0.5 hour and held at this temperature for 5 hours. After cooling to 100°, the crude pigment was isolated by filtration and washed with methanol.[18] The β-modification, thus obtained, may be ground to a finely divided pigment by the finishing method, disclosed in reference,[19] *e.g.*, by milling the crude pigment with sodium chloride and tetrahydronaphthalene.

α-Nickel Phthalocyanine.—A mixture of 120 g. of phthalic anhydride, 180 g. of urea, 49.7 g. of nickel chloride hexahydrate, 0.5 g. of ammonium molybdate and 200 ml. of trichlorobenzene was heated to 200° and agitated at this temperature for 4.5 hours. The reaction mass was cooled to 100°, filtered and the filter cake was placed in a steam still together with one liter of water and 110 ml. of 30% sodium hydroxide. The trichlorobenzene was removed by steam distillation and the crude pigment (β-form) was extracted with 1% hydrochloric acid at 70° for 1.5 hours, filtered, washed and dried. The dry product was then extracted with acetone in a soxhlet apparatus. Twenty grams of the extracted dry powder was milled with 180 g. of dry sodium chloride and 1800 g. of $^3/_8$-inch steel balls for 72 hours at 70 r.p.m. The salt was removed by extraction with 1% aqueous hydrochloric acid at 70°. The isolated pigment contained 9.82% Ni. Calcd. for $C_{32}H_{16}N_8Ni$: Ni, 10.28; yield 82%.

β-Nickel Phthalocyanine.—The crude phthalocyanine, which served as starting material for the α-form, was subjected to the finishing method described in reference 19, *e.g.*, to milling with sodium chloride and tetrahydronaphthalene. A finely divided β-nickel phthalocyanine was obtained.

α-Zinc Phthalocyanine.—A mixture of 128 g. of phthalonitrile, 18.0 g. of zinc powder, and 450 ml. of trichloroben-

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[14] R. H. Wiswall, *Jr.*, U. S. Patent 2,486,351 (issued 10-25-49).

[15] E. A. Hammand and E. Van Norman, *J. Appl. Physics*, **19**, 1097 (1948).

[16] W. C. McCrone, *Anal. Chem.*, **21**, 421, 1016 (1949).

[17] David N. Kendall, abstracts of papers read at A. C. S. Meeting, Boston, Mass., April, 1951, Division of Physical and Inorganic Chemistry, p. 2P.

[18] H. T. Lacey, U. S. Patent 2,318,787 (issued 1-13-50).

[19] D. P. Graham, U. S. P. 2,556,730 (issued 6-12-51).

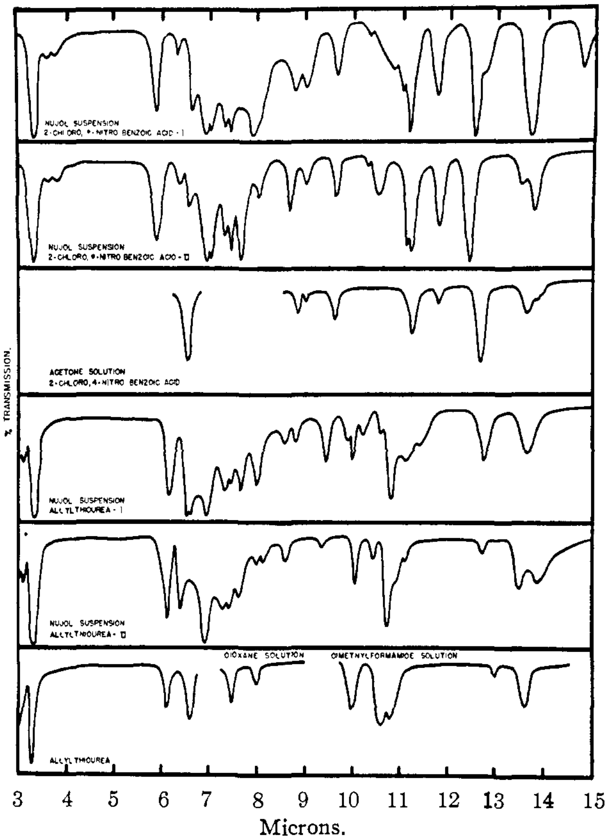

Fig. 5.—Infrared spectra showing variations between spectra of the polymorphic forms of a compound, solid phase. The modifications in solution give identical spectra.

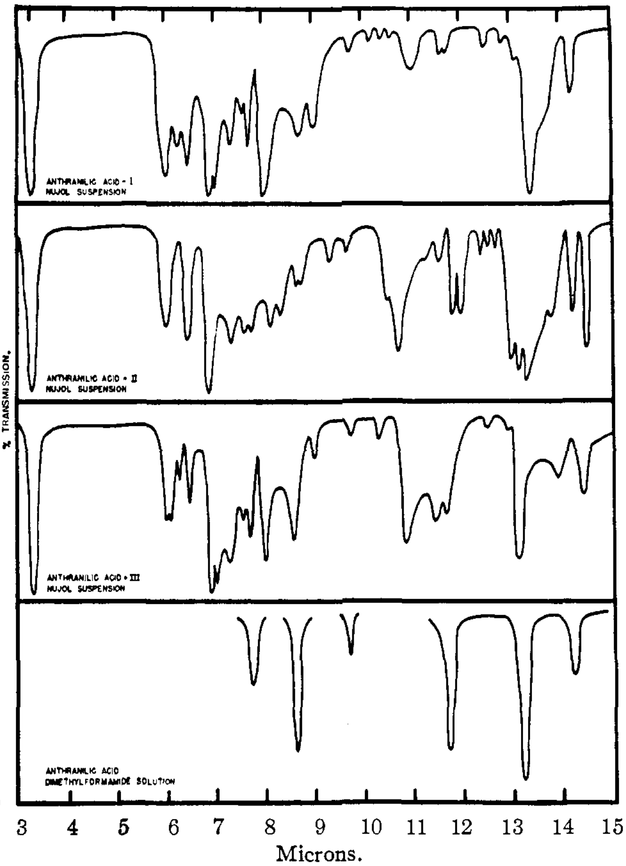

Fig. 6.—Infrared spectra showing the variations occurring among three polymorphic forms of a compound. In solution, all three give identical spectra.

zene was heated to 200° over the period of one hour and kept agitated at that temperature for 12 hours. The reaction mass was allowed to cool to 100°, was filtered, and the filter cake was extracted with cold trichlorobenzene, then with warm ethyl alcohol to remove unreacted phthalonitrile. The product was then twice extracted with 1.5 liters of water, containing 42 ml. of concentrated hydrochloric acid, at 70° for 1.5 hours to remove all excess zinc metal and zinc oxide. The isolated dried pigment was pure; yield 25%. Found: Zn, 11.19; N, 19.13. Calcd. for $C_{32}H_{16}N_8Zn$: Zn, 11.32, N, 19.40. This was the β-modification. The α-modification was obtained by milling the pigment with dry sodium chloride, in the manner described in detail under α-nickel phthalocyanine.

β-Zinc Phthalocyanine.—The transition of α- to β-zinc phthalocyanine was very easily effected by heating the α-form for 8 hours in boiling acetone.

Cobalt Phthalocyanine.—The β-modification was synthesized by reacting finely divided cobalt metal with phthalonitrile in ethylene glycol at 190°. When the pigment was ball-milled with sodium chloride, the α-form was obtained. Although the cobalt phthalocyanine was not as pure as the other phthalocyanines described in this paper, it is believed to be satisfactory for our purpose.

Metal-free Phthalocyanine.—Phthalocyanine may be synthesized by any of the conventional methods. We used the phthalonitrile fusion with cyclohexylamine as reducing agent and followed reference 20. The α-modification was obtained by milling the crude pigment with sodium chloride as described in detail under α-nickel phthalocyanine. The β-modification was obtained by following the finishing method, disclosed in reference,[21] *e.g.*, by milling the pigment with sodium chloride and xylene.

2-Chloro-4-nitrobenzoic Acid.—Modification I was produced by crystallization from benzene. Modification II formed from the slowly cooling melt of the acid.

Allylthiourea.—Modification I (Eastman Kodak Co.) was obtained by crystallization from solvents and Modification II by crystallization from the melt.

Anthranilic Acid.—Anthranilic acid of du Pont manufacture consisted principally of Modification II. Crystallization from water produced Modification I, and from the melt, Modification III was obtained.

Instruments.—The X-ray diffraction patterns were obtained with a Norelco Geiger counter X-ray spectrometer employing nickel filtered radiation from a copper target tube. The samples were in the form of dry powders held in a recessed block of "Lucite" acrylic resin.

The infrared spectra were produced by a Perkin–Elmer single-beam spectrometer (model 12C) using rock salt optics. All the crystalline samples were ground in Nujol and scanned in an 0.025-mm. cell. The solutions, used in the infrared, of 2-chloro-4-nitrobenzoic acid, allylthiourea and anthranilic acid were made up in concentrations of about 10% and were scanned in an 0.12-mm. cell.

The solutions of α- and β-copper phthalocyanines used in the ultraviolet region were prepared by agitating the crystalline sample in α-chloronaphthalene at room temperature and clarifying the solution by filtering through one inch of #209 Celite. The filtered solutions were clear and gave no perceptible Tyndall effect.

Discussion of Figures.—The X-ray diffraction patterns are shown in order to characterize the polymorphic crystal modifications whose infrared spectra were measured. The distinctive patterns of Figs. 1 and 2 show that the crystals of all investigated modifications were well developed, excepting those of cobalt phthalocyanine. The infrared spectra of the phthalocyanines in suspension in Nujol are shown in Figs. 3 and 4. The strong bands at 3.4, 6.85 and 7.25 microns in the suspension spectra in Figs. 3, 4, 5 and 6 are due pri-

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(20) W. L. Rintelman, U. S. Patent 2,485,167 (issued 10-19-49).

(21) O. Stallmann, U. S. Patent 2,556,729 (issued 6-12-51).

marily to Nujol absorption. There is marked similarity between the modifications of the same compound in the 3–8 micron region with noticeable differences occurring among the skeletal frequencies, particularly in the range of 12.5 to 14.5 microns.

α-Copper phthalocyanine, when suspended in cyclohexanol, undergoes transition to the β-form. This was followed, at room temperature, by the change in infrared absorption as recorded in Table I.

TABLE I

Time in minutes	β-form by I.R., %
0	20
30	75
60	90
90	100

Because of the insolubility of the phthalocyanines, we have not been able to obtain satisfactory spectra of their solutions in the infrared. However, copper phthalocyanine shows a limited solubility in α-chloronaphthalene so that the visible and a portion of the ultraviolet region could be scanned. The spectra obtained in this region were identical for both the α- and β-modifications in solution.

The infrared spectra of the crystal modifications of 2-chloro-4-nitrobenzoic acid, allylthiourea and anthranilic acid were also investigated (Figs. 5 and 6). Each modification was scanned in suspension in Nujol as well as in solution. Marked differences are apparent between the spectra of the different modifications in Nujol of any one compound. The solution spectra are not complete because of the limited choice of solvents available. For each compound, an effort was made to obtain a solvent to cover that region of the spectrum where the crystal modifications in suspension showed the greatest differences. In that region, the spectra were found to be identical for all the modifications of the compound in solution.

WILMINGTON, DELAWARE

[FROM THE SLOAN-KETTERING INSTITUTE FOR CANCER RESEARCH]

Preparation of Δ^{20}-Enol Acetates from 20-Ketosteroids[1a]

BY HUBERT VANDERHAEGHE,[1b] E. R. KATZENELLENBOGEN, KONRAD DOBRINER[1c] AND
T. F. GALLAGHER

RECEIVED OCTOBER 29, 1951

Three 20-ketosteroids, 3α,12α-dihydroxypregnane-20-one, 3β-hydroxy-Δ^{5}-pregnene-20-one and 3β-hydroxyallopregnane-20-one, when treated with isopropenyl acetate and sulfuric acid yielded Δ^{20}-20-enol acetates. The structure of the products was shown by color reaction with tetranitromethane, ozonolysis and the preparation of derivatives, and by infrared spectrometry.

When 20-ketosteroids are heated with acetic anhydride in the presence of *p*-toluenesulfonic acid, enol acetates are formed with the unsaturated bond between carbons 17 and 20. The structure of these enol esters has been firmly established by ozonolysis to 17-ketosteroids[2] and by perbenzoic acid oxidation in high yield to 17,20-epoxy-20-acetates.[3] Isopropenyl acetate has been recommended as especially suitable for the preparation of enol acetates,[4] affording excellent yields of product in a smooth reaction, and it was therefore of interest to investigate this reagent with steroid ketones. The first studies were carried out with 3α,12α-diacetoxypregnane-20-one (I) since the enol acetate of this compound prepared by the method of Bedoukian[5] is obtained in high yield as a single geometric isomeride that can be readily crystallized. When I was heated with isopropenyl acetate in the presence of catalytic amounts of sulfuric acid, a new compound was obtained in very good yield. From its infrared spectrum, elementary analysis and saponification equivalent, the product was unquestionably an enol acetate. It was initially believed that this compound was the hitherto undescribed *cis*-geometric isomer since upon treatment with acetic anhydride in the presence of *p*-toluenesulfonic acid it was readily converted to the higher melting enol acetate previously described. In order to test this supposition the same reaction was applied to 3β-hydroxy-Δ^{5}-pregnane-20-one (III), since this substance affords a crystalline mixture of the two geometric isomerides of $\Delta^{5;17,20}$-pregnadiene-3β,20-diol acetate both of which have been separated and well characterized.[6] These known geometric isomers have the following constants: enol acetate "A," m.p. 147°, $[\alpha]_D$ $-50°$; enol acetate "B," m.p. 171–172°, $[\alpha]_D$ $-52°$. The enol acetate obtained with isopropenyl acetate had m.p. 125–126°, $[\alpha]_D$ $-47°$, and the analysis was correct for $C_{25}H_{36}O_4$. Since the rotation of all three products was so similar it was possible that one or more was a polymorphic crystal modification of another but infrared spectrometry in solution proved conclusively that all three were different substances and that all were enol acetates.[7] From this evidence the conclusion was inescapable that one of the products must be the Δ^{20}-enol ester.

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(1) (a) This investigation was supported by grants from the Anna Fuller Fund, the Lillia Babbit Hyde Foundation, and the National Cancer Institute, United States Public Health Service. (b) Fellow of the Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture, Belgium; (c) deceased March 10, 1952.

(2) C. W. Marshall, T. H. Kritchevsky, S. Lieberman and T. F. Gallagher, THIS JOURNAL, **70**, 1837 (1948).

(3) T. H. Kritchevsky and T. F. Gallagher, *ibid.*, **73**, 184 (1951); B. A. Koechlin, T. H. Kritchevsky and T. F. Gallagher, *ibid.*, **73**, 189 (1951).

(4) H. J. Hagemeyer and D. C. Hull, *Ind. Eng. Chem.*, **41**, 2920 (1949).

(5) P. Z. Bedoukian, THIS JOURNAL, **67**, 1430 (1945).

(6) L. F. Fieser and Huang-Minlon, *ibid.*, **71**, 1840 (1949).

(7) We are indebted to Dr. Fieser and Dr. Huang-Minlon for supplying us with an authentic sample of enol acetate "B" for this comparison.