then sought in a higher molecular weight acyl derivative of 3-aminopyridine which could be nitrosated and then extracted from the aqueous nitrosating mixture. The isobutyryl derivative was chosen since it should be less water-soluble than the acetyl compound, and especially since, among various N-nitrosoacylanilides, the isobutyryl derivative was found to be the most reactive.[16]

Isobutyric anhydride and 3-aminopyridine gave a good yield of N-(3-pyridyl)-isobutyramide which was nitrosated with nitrosyl chloride, and the product was easily extracted from the diluted solution with ether or benzene. On warming in benzene, decomposition occurred and a 39% yield of 3-phenylpyridine was isolated. Its properties agreed well with those reported for material isolated, by picrate fractionation, from reactions giving the three isomeric phenylpyridines. Gillam, Hey and Lambert[17] have measured the absorption spectrum of a sample of 3-phenylpyridine which they state may have been (but most probably was not) a mixture. Their spectrum agrees quite well with what we find for isomer-free 3-phenylpyridine (Fig. 1). There is a maximum at 246 mμ (log ε 4.1) and a shoulder in the region of 276 mμ (log ε 3.8) (reported[17] 246 mμ, log ε 4.2; 275 mμ, log ε 4.0). In addition, we find a minimum at 224 mμ (log ε 3.8).

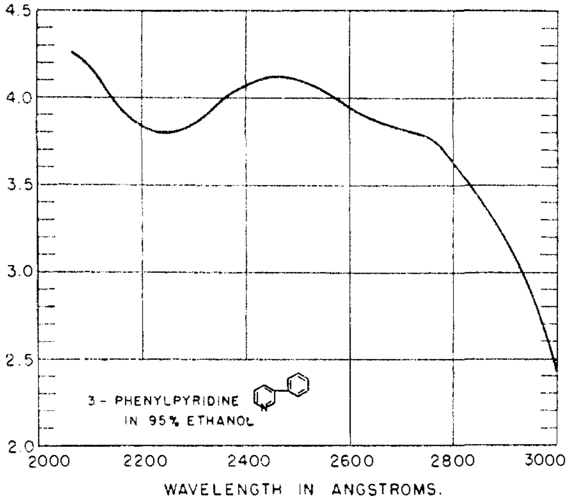

Fig. 1.—Ultraviolet absorption spectrum of 3-phenylpyridine ($5.7 \times 10^{-5}$ *M*) in 95% ethanol at 25°; cell length, 1 cm.

### Experimental[18]

**3,3-Dimethyl-1-(3′-pyridyl)-triazene.**—A solution of 7.0 g. (0.10 mole) of sodium nitrite in 40 ml. of water was added during 15 minutes to a stirred solution of 9.4 g. (0.10 mole) of 3-aminopyridine[19] and 28 ml. of 36 *N* sulfuric acid in 100 ml. of water maintained at 0 to 2°. After an additional 15 minutes at this temperature, the cold diazonium sulfate solution was added to a cooled (0 to 5°), stirred solution of dimethylamine (22.1 ml. of 5.2 *N* aqueous solution, 0.11 mole) in 267 ml. of 2.2 *N* potassium carbonate. Stirring and cooling were continued for 30 minutes, followed by extraction with four 250-ml. portions of ether. Drying the combined ether extracts over sodium hydroxide and distilling gave 10.9 g. (73%) of triazene, b.p. 126–129° (9–10 mm.), $n^{25}$D 1.6093.

*Anal.* Calcd. for $C_7H_{10}N_4$: C, 56.0; H, 6.7; N, 37.3. Found: C, 56.3; H, 6.5; N, 36.9.

The picrate was prepared with ethanolic picric acid and was recrystallized from ethanol, m.p. 141–142°.

*Anal.* Calcd. for $C_{13}H_{13}O_7N_7$: C, 41.2; H, 3.5; N, 25.9. Found: C, 41.3; H, 3.4; N, 25.6.

**N-(3-Pyridyl)-isobutyramide.**—To 10.0 g. (0.11 mole) of 3-aminopyridine was added, slowly and with cooling, 25.2 g. (0.16 mole) of isobutyric anhydride.[20] The mixture, protected from atmospheric moisture, was allowed to stand at room temperature for one hour and then heated on the steam-bath for one-half hour, after which butyric acid and excess anhydride were removed at the water-pump (bath temperature up to 100°). The residue, dissolved in 200 ml. of chloroform, was washed with saturated sodium bicarbonate until the washings were basic to litmus, followed by four 50-ml. portions of water, and then distilled after drying over sodium sulfate. The product boiled at 159–162° (1.5 mm.) and solidified in the receiver. Recrystallization of the 14.7 g. (85%) of distillate from benzene–methylcyclohexane (4 ml. of each per gram) gave 14.1 g. (81% yield) of N-(3-pyridyl)-isobutyramide, m.p. 78–79°.

*Anal.* Calcd. for $C_9H_{12}ON_2$: C, 65.8; H, 7.4; N, 17.1. Found: C, 66.2; H, 7.1; N, 17.3.

**3-Phenylpyridine.**—To a suspension of 20 g. (0.12 mole) of N-(3-pyridyl)-isobutyramide in 125 ml. of glacial acetic acid and 55 ml. of acetic anhydride, to which had been added 55 g. of anhydrous potassium acetate and 2 g. of phosphorus pentoxide, stirred at 0°, was added dropwise 8.0 g. (0.12 mole) of nitrosyl chloride (as a 25% solution in acetic anhydride). Stirring was continued for 10 minutes after the addition and the yellow solution was then poured into 500 ml. of ice and water and extracted with three 250-ml. portions of cold benzene. Anhydrous magnesium sulfate and sodium carbonate were added to the combined extracts which were maintained at 50° until gas evolution ceased. After filtering, the reaction mixture was heated under reflux for two hours, again treated with magnesium sulfate and sodium carbonate, filtered, and distilled to give 7.3 g. (39%) of 3-phenylpyridine, b.p. 117–118° (5 mm.), $n^{25}$D 1.6123 (reported[5] b.p. 269–270° (749 mm.)).

*Anal.* Calcd. for $C_{11}H_9N$: C, 85.1; H, 5.9; N, 9.0. Found: C, 84.7; H, 5.9; N, 9.0.

The picrate, after crystallization from ethanol, melted at 159–160° (reported[5] m.p. 161–163.5°).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

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[16] R. Huisgen and L. Krause, *Ann.*, **574**, 157 (1951).

[17] A. E. Gillam, D. H. Hey and A. Lambert, *J. Chem. Soc.*, 364 (1941).

[18] All melting points are corrected; microanalyses were performed by the Microchemical Laboratory, University of California.

[19] C. F. H. Allen and C. N. Wolf, *Org. Syntheses*, **30**, 3 (1950).

[20] W. Gerrard and A. M. Thrush, *J. Chem. Soc.*, 741 (1952).

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## Unit Cell Constants of α-Copper Phthalocyanine

BY MARK T. ROBINSON AND GILBERT E. KLEIN

RECEIVED AUGUST 28, 1952

Although the dimorphism of copper phthalocyanine ($C_{32}H_{16}N_8Cu$) has been reported,[1] no unit cell constants have been published for the α (metastable) modification of the pigment. The β (stable) modification has been thoroughly discussed by Robertson.[2] In connection with another study we have had occasion to make an analysis of the structure of α-$C_{32}H_{16}N_8Cu$.

The material used was prepared from Solfast Sky Blue[3] by dissolving in 98% $H_2SO_4$, filtering to remove any residue, and precipitating α-$C_{32}H_{16}N_8Cu$ by pouring the solution slowly into a large volume of water. The dark blue precipitate was filtered with suction and thoroughly washed with

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[1] A. A. Ebert and H. B. Gottlieb, THIS JOURNAL, **74**, 2806 (1952); Publication Board Report 74892 (1947), pp. 9060-1.

[2] J. M. Robertson, *J. Chem. Soc.*, 615 (1935); R. P. Linstead and J. M. Robertson, *ibid.*, 1736 (1936).

[3] Sherwin-Williams Co. trademark for their brand of $C_{32}H_{16}N_8Cu$.

acetone. The solid was dried in a high air velocity hood and finely ground.

X-Ray diffraction patterns were recorded both on a North American Philips High Angle Spectrometer and with a 114.59-mm. diameter powder camera using Ni filtered Cu radiation (λ 1.5418 Å.). The 29 lines obtained and the planes to which they are attributed are listed in Table I. The tetragonal unit cell constants derived from the patterns are listed in Table II. Using these constants, *d* values were calculated which agreed with the observed values to better than 1%. The density of the pigment was determined by water displacement in a 25-ml. pycnometer.

TABLE I

THE X-RAY DIFFRACTION PATTERN OF $\alpha$-$C_{32}H_{16}N_8Cu$

| (*hkl*) | *d*, Å. | $I/I_0$ | (*hkl*) | *d*, Å. | $I/I_0$ |
|---|---|---|---|---|---|
| 001 | 12.790 | 1.0 | 610 | 2.836 | 0.3 |
| 110 | 12.190 | 0.9 | 620 | 2.722 | .2 |
| 200 | 8.630 | .4 | 005 | 2.532 | .2 |
| 201 | 7.196 | .1 | 613 | 2.365 | .1 |
| 002 | 6.417 | .1 | 524 | 2.254 | .1 |
| 310 | 5.490 | .7 | 444 | 2.229 | .2 |
| 320 | 4.796 | .1 | 006 | 2.118 | .5 |
| 400 | 4.353 | .1 | 661 | 2.037 | .1 |
| 330 | 4.068 | .1 | 900 | 1.935 | .2 |
| 411 | 3.678 | .7 | 007 | 1.848 | .1 |
| 500 | 3.486 | .7 | 770 | 1.757 | .4 |
| 510 | 3.395 | .9 | 904 | 1.651 | .2 |
| 520 | 3.226 | .9 | 881 | 1.523 | .1 |
| 342 | 3.100 | .2 | 009 | 1.421 | .1 |
| 333 | 2.931 | .2 | | | |

TABLE II

UNIT CELL CONSTANTS OF $\alpha$-$C_{32}H_{16}N_8Cu$

$a_0 = 17.367$ Å.
$c_0 = 12.790$ Å.
$Z = 6$ ($C_{32}H_{16}N_8Cu$)
$d_{\text{calcd.}} = 1.488$ g./cm.$^3$
$d_{\text{measd.}} = 1.49$ g./cm.$^3$
Probable space group $C^1_{4h}$ − P4/m

SOLID STATE DIVISION
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE

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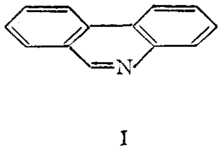
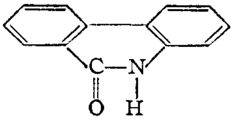
## A New Synthesis of Phenanthridine[1]

BY E. C. TAYLOR, JR., AND A. E. MARTIN

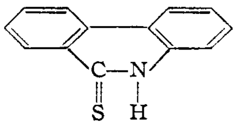
RECEIVED AUGUST 11, 1952

Phenanthridine (I) has been prepared from phenanthridone (II) by distillation with zinc dust,[2] by reduction with lithium aluminum hydride in 70% yield,[3] and by conversion to 9-bromophenanthridine in unspecified yield[4] followed by dehalogenation with hydrogen and Raney nickel.[5] The first method is of theoretical rather than practical interest; the second is not suitable for the preparation of large quantities of phenanthridine, and the amount of lithium aluminum hydride must be carefully controlled to avoid formation of 9,10-dihydrophenanthridine[6]; and the third requires phosphorus oxybromide, which is not readily available. Attempts to prepare phenanthridine by dehalogenation of the more readily prepared 9-chlorophenanthridine gave 9,10-dihydrophenanthridine.[6] It has been stated recently that "there seems to be no really satisfactory method for the conversion of phenanthridone into phenanthridine on a large scale."[6]


I


II

Phenanthridine has now been prepared from phenanthridone in 89.5% over-all yield by conversion to the previously unknown phenanthridinethione (III) followed by desulfurization with Raney nickel in dimethylformamide–ethanol solution. This method is suitable for large scale preparations, and the phenanthridine thus obtained is free of the 9,10-dihydro derivative.


III

### Experimental[7]

**Phenanthridinethione.**—A mixture of 20 g. of phenanthridone, 30 g. of phosphorus pentasulfide and 300 ml. of pyridine was heated under reflux for two hours. The reaction mixture was then poured into one liter of water, and the precipitated yellow solid was separated by filtration, washed thoroughly with water and recrystallized from aqueous dimethylformamide. The phenanthridinethione (20.3 g., 94%) was obtained in the form of long, yellow needles, m.p. 281–283°. The analytical sample was prepared by sublimation at 200° (1 mm.).

*Anal.* Calcd. for $C_{13}H_9NS$: C, 73.9; H, 4.3; N, 6.6. Found: C, 74.2; H, 4.5; N, 6.5.

**Phenanthridine.**—A mixture of 30 g. of phenanthridinethione, 120 g. (weighed wet with water) of Raney nickel catalyst,[8] 300 ml. of dimethylformamide and 300 ml. of ethanol was heated under reflux for one hour. The colorless solution, exhibiting a strong blue fluorescence, was filtered, and the filtrate acidified with hydrochloric acid and evaporated to dryness under reduced pressure. The residue was dissolved in 100 ml. of water, the solution treated with Norit and the filtrate made alkaline with aqueous ammonium hydroxide. Upon standing, phenanthridine (24.1 g., 95%) separated as a white crystalline mass; m.p. 99–100°. One recrystallization from aqueous acetone gave colorless plates of pure phenanthridine, m.p. 106°.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

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(1) For recent reviews on phenanthridine syntheses, see (a) L. P. Walls in "Heterocyclic Compounds," Vol. IV, edited by R. C. Elderfield, John Wiley and Sons, Inc., New York, N. Y., 1952, p. 564; (b) R. S. Theobald and K. Schofield, *Chem. Revs.*, **46**, 171 (1950); (c) E. A. Braude and J. S. Fawcett, *J. Chem. Soc.*, 3113 (1951).

(2) A. Pictet and H. J. Ankersmit, *Ann.*, **266**, 138 (1891).

(3) P. de Mayo and W. Rigby, *Nature*, **166**, 1075 (1950).

(4) L. P. Walls, *J. Chem. Soc.*, 104 (1934).

(5) A. Albert, D. J. Brown and H. Duewell, *ibid.*, 1284 (1948).

(6) G. M. Badger, J. H. Seidler and B. Thompson, *ibid.*, 3207 (1951).

(7) All melting points are corrected. Microanalyses were carried out by Mrs. Katherine Pih, Mrs. Esther Fett and Mr. Joseph Nemeth.

(8) A commercially available grade of Raney nickel catalyst in water (Raney Catalyst Co., Chattanooga, Tennessee) was employed. Less catalyst was necessary and a shorter reaction time was possible when fresh Raney nickel (D. J. Brown, *J. Soc. Chem. Ind.*, **69**, 353 (1950)) was employed.