dropwise, to a stirred solution of isopropylmagnesium chloride which had been prepared from 48.6 g. (2.0 g.-atoms) of magnesium, 157.1 g. of isopropyl chloride, 750 ml. of ether, and 4 ml. of ethyl bromide. The mixture was stirred and refluxed for 20 hr.

Iodine (126.9 g., 0.5 mole), dissolved in 1000 ml. of ether, was added, dropwise, to the stirred mixture. After the material had been stirred for 140 hr., it was poured into a mixture of 167 ml. of concd. hydrochloric acid, ice, and 1000 ml. of water and then stirred for an hour. The layers were separated, the aqueous layer was extracted with benzene, and the solvents were removed from the combined organic solutions in a stream of air. The crystalline material was filtered and exposed to air for several days to remove traces of iodine. The product, after recrystallization from acetic acid, weighed 75.0 g. (55%); m.p. 239–240°.[3]

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22; neut. equiv., 135.1. Found: C, 71.12; H, 5.52; neut. equiv., 135.8.

N,N,N',N'-Tetramethyl-α,α'-diphenylsuccindiamide. N,N-Dimethylphenylacetamide[4] (32.6 g.), dissolved in 250 ml. of ether, was added, dropwise, to a stirred solution of isopropylmagnesium chloride prepared from 4.8 g. of magnesium, 16.5 g. of isopropyl chloride, 500 ml. of ether, and 4 ml. of ethyl bromide. Iodine (25.4 g.), dissolved in 250 ml. of ether, was added, dropwise, to the stirred mixture followed by the addition of 500 ml. of benzene. The material was stirred and refluxed for 3 hr. and then stirred for 20 hr. at room temperature. After the addition of a mixture of 16 ml. of concd. hydrochloric acid and 500 ml. of ice water, the layers were separated, and the solvents were removed from the organic layer in a stream of air. The brown residue became crystalline after trituration with acetone. The product, after recrystallization from ether, weighed 7.9 g. (24%); m.p. 193–194°.

Anal. Calcd. for $C_{20}H_{24}O_2N_2$: C, 74.04; H, 7.46; N, 8.64. Found: C, 74.02; H, 7.30; N, 8.46.

N,N-Dibenzylphenylacetamide. Dibenzylamine (197.3 g.) was dissolved in 1 l. of ether, the solution was stirred and 58.8 g. of phenylacetyl chloride[5] was added, dropwise. After the mixture had been stirred for 4 hr., the precipitated dibenzylamine hydrochloride was filtered. Removal of the solvent from the filtrate yielded 83.2 g. (69%) of product; m.p. 64–65° after recrystallization from ether.

Anal. Calcd. for $C_{22}H_{21}ON$: C, 83.77; H, 6.71. Found: C, 83.78; H, 6.66.

N,N,N',N'-Tetrabenzyl-α,α'-diphenylsuccindiamide. This compound was obtained in 15% yield from N,N-dibenzylphenylacetamide by the process described above; m.p. 172–173° after recrystallization from ether.

Anal. Calcd. for $C_{44}H_{40}O_2N_2$: C, 84.04; H, 6.41. Found: C, 83.99; H, 6.19.

2,3-Diphenyl-1,4-butanediol. Lithium aluminum hydride (5.9 g.) was suspended in 750 ml. of ether, stirred and a suspension of 21.6 g. of *meso-α,α'*-diphenylsuccinic acid in 750 ml. of ether was added slowly. The mixture was stirred for 24 hr., cooled, stirred, and 12 ml. of water was added, dropwise. After filtration, the solvent was removed from the filtrate and the residue was recrystallized from benzene; yield 10.8 g. (55%); m.p. 143–144°.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.27; H, 7.54.

Isolation of 3,4-diphenyltetrahydrofuran from the attempted preparation of 5,6-diphenyl-2-bromomethyl-1,3-dioxolane. A mixture of 9.7 g. (0.04 mole) of 2,3-diphenyl-1,4-butanediol, 7.9 g. (0.04 mole) of bromoacetal, 1 ml. of concd. hydrochloric acid and 1 ml. of concd. sulfuric acid was placed in a Claisen flask and heated in an oil bath. As the bath temperature was raised slowly from 95–150°, an unidentified liquid distilled. The residue was then distilled under reduced pressure; b.p. 142° (0.9 mm.). The distillate solidified rapidly and was recrystallized from ethanol; m.p. 86–88°; yield 3.5 g. (39%).

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.67; H, 7.07.

College of Pharmacy
University of Michigan
Ann Arbor, Mich.

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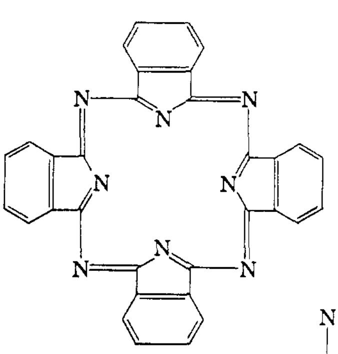
Structure of Phthalocyanine[1]

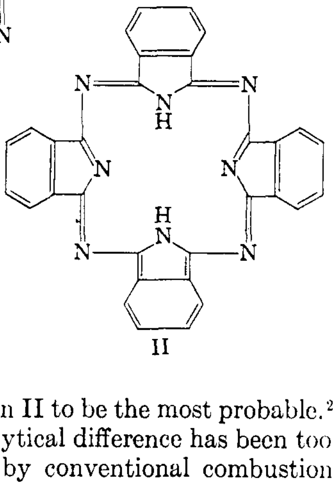
Norman A. Frigerio

Received August 15, 1960

Of the two suggested formulas for phthalocyanine $(C_8H_4N_2)_4$ (I) or $(C_8H_4N_2)_4H_2$ (II) various lines of evidence have shown II to be the most probable.[2] Nevertheless, the analytical difference has been too small to be resolved by conventional combustion techniques, and a direct demonstration of Formula II is lacking.



I



II

In developing syntheses of deuterio-phthalocyanine we have obtained analyses which show that $^2/_{18}$ of the total hydrogens are easily replaced by deuterium under conditions such that copper phthalocyanine shows no exchange. This is taken to indicate that there are 18 hydrogen atoms per mole and that two of them differ chemically from the others in accord with formula II.

An infrared peak at 3298 cm.$^{-1}$ has been reported for phthalocyanine and attributed to two

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(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) R. P. Linstead and A. R. Lowe, *J. Chem. Soc.*, **1934**, 1031; C. E. Dent, R. P. Linstead, and A. R. Lowe, *J. Chem. Soc.*, (1033).

TABLE I

Summary of Analytical Results

	C	N	Cu	Combustion Water	Atom D
Calcd. for $(C_8H_4N_2)_4H_2$	74.69	21.78		31.51	0.016
Found	74.74	21.82		31.44	0.016
Calcd. for $(C_8H_4N_2)_8$ Cu	67.18	19.45	11.03	25.02	0.016
Found	67.23	19.51	11.02	24.96	0.016
Found for $(C_8H_4N_2)_4$ Cu treated with D_2SO_4 and D_2O	67.20	19.48	11.01	25.00	0.065
Calcd. for $(C_8H_4N_2)_4$ D_2	74.40	21.69		31.78	11.11
$(C_8H_4N_2)_4D_2$ obtained from $(C_8H_4N_2)_4H_2$					
5th crystallization	74.40	21.70		31.74	11.10
6th crystallization	74.43	21.66		31.79	11.12
$(C_8H_4N_2)_4D_2$ obtained from $(C_8H_4N_2)Li_2$					
5th crystallization	74.42	21.63		31.80	11.10
6th crystallization	74.44	21.68		31.77	11.09

pyrrole NH bonds.[3] Since a band at this frequency has also been observed for copper phthalocyanine,[4] it would appear unlikely that it is assignable to NH. If such an NH bond were present one would expect to find an ND bond peak at 2333 cm.$^{-1}$ in deuterio-phthalocyanine with concomitant disappearance of the 3298 cm.$^{-1}$ peak. We observed a weak band at 3298 cm.$^{-1}$ in phthalocyanine, deuterio-phthalocyanine, and copper phthalocyanine but failed to observe any peaks in the region 1700 to 3200 cm.$^{-1}$ in the spectra of the deuterio-phthalocyanine, its spectra being identical to that of phthalocyanine over the range 850 to 4000 cm.$^{-1}$

EXPERIMENTAL

Dilithium phthalocyanine was prepared according to Barrett,[5] and recrystallized from anhydrous acetone–benzene to constant analysis.

Phthalocyanine was prepared from dilithium phthalocyanine by solution in 100% sulfuric acid followed by dilution with water,[5] at 0°, and recrystallized from sulfuric acid–water to constant analysis.

Copper phthalocyanine was prepared from dilithium phthalocyanine and anhydrous cupric chloride[5] and recrystallized from sulfuric acid–water, at 0°, to constant analysis.

Deuterio-phthalocyanine (method 1) was prepared from dilithium phthalocyanine by solution in 100% deutero sulfuric acid followed by dilution with deuterium oxide at 0° and recrystallized from deuterosulfuric acid–deuterium oxide to constant analysis.

Deuterio-phthalocyanine (method 2) was prepared from phthalocyanine by solution in 100% deutero sulfuric acid followed by dilution with deuterium oxide at 0°, and recrystallized from deutero sulfuric acid–deuterium oxide to constant analysis.

Sulfuric acid and deutero sulfuric acid were prepared by cautious addition of the stoichiometric amount of water, or deuterium oxide, to sulfur trioxide. All deuterium oxide used was contaminated with 0.13% protium.

Infrared spectra were run on potassium bromide disks in a Beckman Model IR-7 at resolutions of 2 cm.$^{-1}$ or better.

X-ray analyses indicated that all phthalocyanine preparations were of the *alpha* crystalline modification.[6,7]

Combustion analyses were performed in duplicate on each of two samples to minimize random errors.

H to D ratio was analyzed on a mass spectrometer. The gas used was obtained by reacting the water of combustion with purified sodium.

Division of Biological and Medical Research
Argonne National Laboratory
Argonne, Ill.

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[3] A. N. Terenin and A. N. Sidorov, *Spectrochim. Acta Suppl. Int. Cong. Spect.* **9**, 574 (1957).

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[5] P. A. Barrett, D. A. Frye, and R. P. Linstead, *J. Chem. Soc.*, **1938**, 1157.

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[7] A. A. Ehret and H. B. Gottlieb, *J. Am. Chem. Soc.*, **74**, 2806 (1952).

Reaction of Malononitrile with Chlorine Near Neutral *p*H

David H. Rosenblatt and Gordon H. Broome

Received August 31, 1960

Addition of two moles of chlorine to a concentrated aqueous solution of malononitrile at 0° was reported[1] to produce an oily product from which dichloromalononitrile (b.p. 97°/754 mm.) and dichlorocyanoacetamide (m.p. 91°; b.p. 150°/15 mm.) were isolated. It is obvious, although not stated by the authors, that the aqueous malononitrile solution became quite acidic as soon as chlorine introduction was begun and that some dichloromalononitrile separated from the reaction mixture before it could react further with chlorine in the aqueous phase.

The chlorination reported here differs from that cited above in that, in the present investigation, a dilute malononitrile solution was added to hypochlorite at an initial *p*H of 7 and ambient temperature, with continual neutralization of acid formed in the reaction, and in the final molar ratio of chlorine to malononitrile of 2.5. While no attempt was made to isolate volatile products, such as those encountered by Ott and co-workers,[1] or to get a quantitative measure of yield, dichloroacetamide was obtained in about 18% and dichloromalondiamide in about 3% of the theoretical amounts. Carbonate was also detected among the products of reaction. This note concerns itself with explaining the origin of the compounds identified, inasmuch as the rapid hydrolysis of nitrile groups to amide and the replacement of one amide function

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[1] E. Ott and B. Löpmann, *Ber.*, **55**, 1255 (1922), corrected by E. Ott and H. Finken, *Ber.*, **58**, 1703 (1925).