indicated an excretion of 68% of the amino acid unchanged and 3.1% of the amino acid appeared as cotinine.

Thermal Lactamization of Synthetic and Metabolic γ-(3-Pyridyl)-γ-methylaminobutyric Acid.—The monohydrate of the methylamino acid[4] (100 mg.) ($[\alpha]^{22}\text{D}$ +17.2) in a Pyrex tube was heated for 0.5 hr. in an atmosphere of nitrogen at 145–150°. The oily residue was extracted with six portions of chloroform (5 ml. each). The product was dissolved in methanol and gave an optical rotation ($[\alpha]^{21.5}_{5461}$ −18.16° (*c* 4.35)).

Fraction C (303 mg.) from the pooled urine of six dogs (893 mg. of administered nicotine) was heated for 0.5 hr. at 145–150° under nitrogen. The residue then was dissolved in 5 ml. of distilled water. The solution was extracted with six portions (5 ml. each) of chloroform. Upon evaporation of the chloroform extract under diminished pressure a residue of cotinine (49.8 mg.) or 5.55% of the dose of nicotine was obtained ($[\alpha]^{30}_{5461}$ −18.77° (*c* 4.98)). In comparison a sample of cotinine prepared from nicotine by the method of Pinner[11] had a specific rotation ($[\alpha]^{30}_{5461}$ −19.85; (*c* 5.59, methanol)).

RICHMOND, VIRGINIA

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

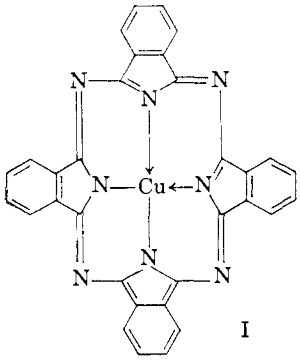
Polymeric Phthalocyanines. II[1]

BY C. S. MARVEL AND MICHAEL M. MARTIN

RECEIVED JUNE 30, 1958

The cocondensation of 3,3′,4,4′-tetracyanodiphenyl ether and phthalonitrile with copper-bronze under phthalocyanine-forming conditions was found to result in the formation of dimeric or trimeric products. No high molecular weight polymeric phthalocyanines were formed. A high molecular weight crosslinked polymer of 3,3′,4,4′-tetracyanodiphenyl ether was prepared by fusion with copper-bronze. Similar results were obtained in the cocondensation in the presence of sodium amylate. All of these polymeric materials underwent decomposition in air at 350°.

Several attempts[2–6] have been made to prepare high molecular weight phthalocyanines by the reaction of a tetrabasic acid derivative with a copper salt, urea and a vanadate or molybdate promoter. In all cases, dark-colored, sulfuric acid-soluble products were obtained which could not be sufficiently purified to allow satisfactory characterization. It is doubtful if these products contain any high polymers. It was felt that since copper phthalocyanine (I) can be prepared in nearly quantitative yield by the fusion of phthalonitrile and copper-bronze, polymer formation should proceed more smoothly to give a more easily purified product in a cocondensation reaction involving phthalonitrile and a tetranitrile. The only impurities should be the unreacted nitriles, which could be extracted with acetone, and unreacted copper-bronze, which could be removed by dissolving the product in sulfuric acid and recovering the phthalocyanine by diluting the solution. With pure materials the structure and molecular weight could be ascertained with a greater degree of confidence.

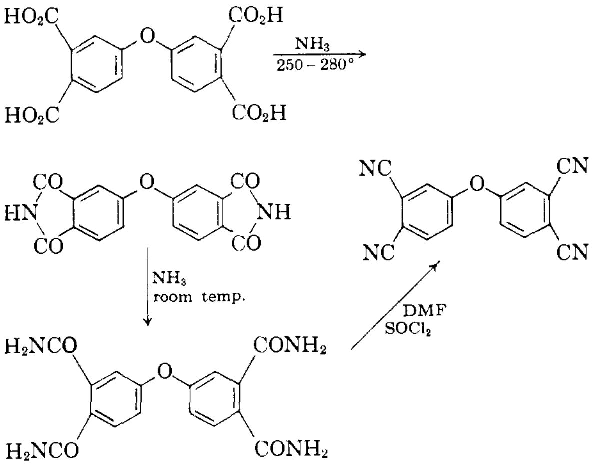


I

Results and Discussion

The synthesis of 3,3′,4,4′-tetracyanodiphenyl ether is outlined in Scheme I. 3,3′,4,4′-Tetracarboxydiphenyl ether, prepared by the method of Marvel and Rassweiler,[6] was converted to the diimide by decomposing the tetraamonium salt at 250–280°. This diimide was converted to the tetraamide by stirring with excess concentrated ammonia. The over-all yield, based on acid, was 85%. This tetraamide was dehydrated with thionyl chloride and dimethylformamide[5] to 3,3′,4,4′-tetracyanodiphenyl ether in 80% yield.

SCHEME I



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[1] This research was supported by Contracts AF 33(616)-3772 and -5486 with the Materials Laboratory of Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, Lt. Paul D. Shaw and Lt. Myron Black, project engineers. Reproduction of this paper in whole or in part is permitted for any purpose of the United States Government. The paper is based on portions of a thesis submitted by Michael M. Martin to the Graduate College of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] (a) Swiss Patent 263,655 (1949); (b) U. S. Patent 2,492,732 (1949).

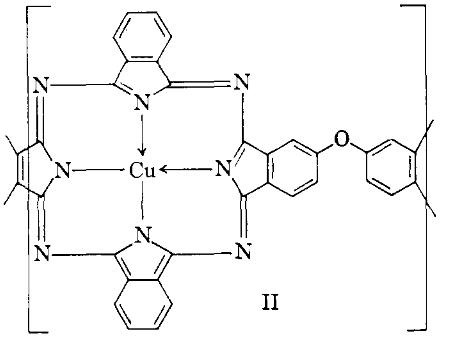
[3] Sprague Electric Co., Final Report under Contract No. DA-36-039-SC-87 to the United States Army Signal Corps, May 14 through October 15, 1952.

[4] W. C. Drinkard, Thesis, Doctor of Philosophy, University of Illinois, 1956.

[5] E. A. Lawton and D. D. McRitchie, WADC Technical Report 57-642, November, 1957.

[6] C. S. Marvel and J. H. Rassweiler, THIS JOURNAL, **80**, 1196 1958).

The expected repeating unit of a linear polymeric copper phthalocyanine from phthalonitrile and 3,3′,4,4′-tetracyanodiphenyl ether is indicated in formula II. Such a structure calls for a ratio of dinitrile to tetranitrile of two to one.



II

The fusion reaction of phthalonitrile and 3,3′,4,4′-tetracyanodiphenyl ether using a variety of molar ratios with copper-bronze at 275° over three hours was investigated. The products were purified by washing with boiling acetone and shaking for 20 hours at room temperature with concentrated sulfuric acid. This operation separated the product into an initially sulfuric acid-soluble fraction and an initially sulfuric acid-insoluble fraction. The cold sulfuric acid-insoluble fraction could be dissolved in hot sulfuric acid and did not precipitate on cooling. All of these materials are dark blue, hygroscopic powders with a beautiful metallic purple reflex as isolated from the reaction mixture. After treatment with sulfuric acid, they are dark blue to green-black in color. Their sulfuric acid solutions are brown to red-brown in contrast to the green color of the monomeric copper phthalocyanine in sulfuric acid. They undergo decomposition in air at 350° over 24 hours.

Infrared data leave little doubt that these materials are phthalocyanines. They have bands at 745, 875, 950, 1050, 1090 and 1120 cm.$^{-1}$. Ebert and Gottlieb[7] report that monomeric phthalocyanines have bands at 750, 885, 952, 1060, 1080 and 1123 cm.$^{-1}$.

Three lines of evidence, infrared spectra, viscosities and elemental analyses, indicate that polymerization progressed to a very low degree in the co-condensation reaction. The infrared spectrum of the product, prior to treatment with sulfuric acid, has an absorption band at 2240 cm.$^{-1}$ due to the unreacted cyano groups. After treatment of this product with concentrated sulfuric acid, absorption bands appear at 1715, 1770 and 1840 cm.$^{-1}$, due to five-membered imide and anhydride groups formed by hydrolysis of the *ortho*-cyano groups. Apparently the higher frequency absorption band of the imide coincides with the lower absorption band of the anhydride, so that only three peaks are observed. Had polymer formation proceeded to a high degree, imide and anhydride absorption would be weak, but these spectra indicate a high concentration of unreacted groups.

In Table I are shown molar ratios of reactants employed, along with the viscosities of the products. The ratio of dinitrile to tetranitrile was varied from 1.00 to 3.00 in an attempt to find the best combination for polymer formation. However, no trend in viscosities was observed. Samples number 1–8 were prepared by fusing the reactants for three hours at 275°. The viscosities range from 0.03 to 0.11. Individual differences are small and probably not too significant. It also should be noted that the viscosities for the hot sulfuric acid-soluble and cold sulfuric acid-soluble fractions are essentially the same, except for sample 7. Thus, it is doubtful that there is any large difference in molecular weights of the two fractions. It is important to note that monomeric copper phthalocyanine has a viscosity of 0.03. Since the tetranitrile is twice the size of phthalonitrile, a monomeric phthalocyanine derived from it probably would have a somewhat larger viscosity. These viscosity data are indicative of a rather low degree of polymerization. Sample 9 is the product obtained from heating sample 5, prior to sulfuric acid treatment, for five hours at 280–300°. It appears from the viscosity values that this treatment resulted in a small but significant increase in molecular weight, although the degree of polymerization is still quite low. Sample 10 is the product of a sealed tube cocondensation in which heating at 275° was continued for 11.25 hours. It is clear that the extended reaction time did not increase the extent of polycondensation.

TABLE I

PROPERTIES OF COCONDENSATION PRODUCTS

Sample	Molar ratio dinitrile/ tetranitrile	Cold sulfuric acid-soluble-fraction % Prod.	Cold sulfuric acid-soluble-fraction η (g./100 ml.)[a]	Hot sulfuric acid-soluble-fraction % Prod.	Hot sulfuric acid-soluble-fraction η (g./100 ml.)[a]
Copper phthalocyanine	....	100	0.03 (0.24)	..	....
1	1.00/1.00	75	.07 (.27)	25	0.05 (0.25)
2	1.50/1.00	69	.05 (.24)	31	.05 (.23)
3	1.90/1.00	45	.05 (.23)	55	.04 (.25)
4	2.00/1.00	38	.04 (.25)	62	.03 (.26)
5	2.10/1.00	74	.07 (.22)	26	.06 (.25)
6	2.20/1.00	23	.06 (.23)	77	.08 (.25)
7	2.50/1.00	64	.05 (.24)	36	.11 (.26)
8	3.00/1.00	100	.05 (.24)	..	....
9	2.10/1.00	57	.08 (.25)	43	.12 (.22)
10	2.10/1.00	80	.06 (.25)	20	.05 (.24)

[a] Viscosities determined in an Ostwald viscosimeter in sulfuric acid solution at 25°.

Phthalocyanines also were prepared by the condensation of 3,3′,4,4′-tetracyanodiphenyl ether in the absence of phthalonitrile. When the reaction was allowed to proceed for three hours at 275°, a sulfuric acid-soluble phthalocyanine was formed with a viscosity of 0.06 (0.24 g./100 ml.), indicating that the polymerization did not proceed to a high degree. However, if heating were continued for 11 hours, a phthalocyanine was formed which was insoluble in concentrated sulfuric acid, indicating that a high molecular weight, crosslinked polymer had been formed. This is the first sulfuric acid-insoluble polymer reported and probably represents the first instance of the formation of a high molecular weight polymeric copper phthalocyanine.

Analytical data further elucidated the structure of these products. In Table II are listed the calcu-

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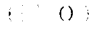
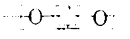
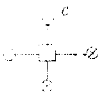
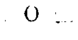
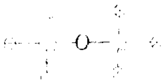
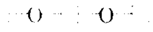
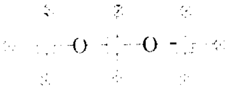
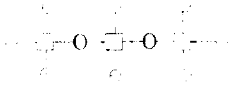
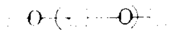
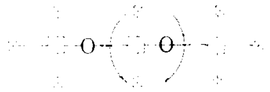
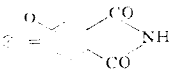
(7) A. A. Ebert and H. B. Gottlieb, THIS JOURNAL, **74**, 2806 (1952).

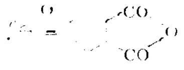
TABLE II

CALCULATED ANALYTICAL VALUES ON POSSIBLE PRODUCTS OF COCONDENSATION REACTION

Structure	Compound	Mol. wt.	N, %	Cu, %
	Copper phthalocyanine	576.10	19.45	11.03
	Linear polymer	(590.08)x	18.99	10.75
	Completely crosslinked polymer	(604.06)x	18.55	10.52
	Monomeric	1220.58	13.77	5.20
	Monomeric	1222.54	11.46	5.20
	Dimeric	1166.18	19.22	10.90
	Dimeric	2132.90	14.45	5.96
	Dimeric	2135.84	12.46	5.95
	Trimeric	1756.26	19.16	10.85
	Trimeric	3045.22	14.72	6.25
	Trimeric	3053.06	11.02	6.24
	Tetrameric	2346.34	19.11	10.83
	Tetrameric	3956.54	14.87	6.42

a = a phthalocyanine nucleus

b 

c 

lated nitrogen and copper values for a number of the possible products of a cocondensation. Clearly, as the degree of polymerization increases, the number of possible products becomes extremely large, and a complete tabulation of analytical values is both prohibitively tedious and confusing. However, comparison of the possible compounds described in Table II with the analytical results given in Table III gives some significant information.

It is impossible to designate a definite structure on the basis of analytical results, but it is possible to eliminate many structures. It can be stated definitely that the cocondensation products are not high molecular weight linear polymers, since both copper and nitrogen are much lower than the calculated values. The data for number 12, the sulfuric acid-insoluble polymer, are consistent with the theoretical values for a completely crosslinked polymer. The nitrogen values for the hot sulfuric acid-soluble fractions are lower than the corresponding cold sulfuric acid-soluble fractions, due to conversion of imide groups to anhydride groups. By comparing the observed copper values with the possible ones, it can be seen that most of the products give values at the lower end of the acceptable range. This observation indicates a high incorporation of tetranitrile, that is, the presence of numerous imide and anhydride groups, which is consistent with infrared data. The degree of polymerization can at best be only approximated, but the copper values especially are indicative of a low chain length. Many of the observed values are less than 6%, which is theoretically possible only for monomeric or dimeric compounds. Thus, from infrared, viscosity and analytical data, it would appear that the product of a cocondensation reaction of phthalonitrile and 3,3',4,4'-tetracyanodiphenyl ether with copper-bronze is a mixture of materials in which polymerization has proceeded no further than the dimer or trimer stage.

A sulfuric acid-soluble condensation product of the tetranitrile was converted to a sulfuric acid-insoluble, crosslinked polyimide by fusion with *m*-phenylenediamine. Polymerization is due to condensation of the diamine with anhydride and imide groups appended to the dimeric or trimeric phthalo-

TABLE III

OBSERVED ANALYTICAL DATA ON COCONDENSATION PRODUCTS

Sample	N,[c] %	Cu, %	Sample	N,[c] %	Cu, %
Copper phthalocyanine	19.09	10.98[d]	12[f]	18.00	10.33[d]
1C[a]	12.77	5.16[d]	1H[b]	9.89	5.08[d]
2C	14.22	5.72[e]	2H	11.56	6.19[d]
3C	13.80	5.70[c]	3H	12.06	6.43[d]
4C	12.17	4.88[e]	4H	11.05	5.54[e]
5C	13.63	7.42[d]	5H	10.02	6.21[d]
6C	15.59	5.59[e]	6H	11.25	5.33[e]
7C	12.21	5.05[e]	7H	12.40	6.18[e]
8C	13.78	6.50[e]	8H	...	...
9C	13.93	7.45[d]	9H	14.56	6.81[d]
10C	15.92	6.96[d]	10H	11.60	6.11[d]
11C[f]	11.88	7.32[e]	11H[f]	11.66	7.92[d]

[a] C denotes cold sulfuric acid-soluble fraction. [b] H denotes hot sulfuric acid-soluble fraction. [c] The standard Dumas method gave very low N values. Satisfactory values are obtained by carrying out the decomposition in the presence of oxygen and copper oxide. [d] Electrolytic analysis. [e] Iodometric analysis. [f] Number 11C and number 11H are the homocondensation products of the tetranitrile which involved a 3-hour reaction time, and number 12 is the crosslinked homopolymer of the tetranitrile formed after 11.25 hours.

cyanine from the condensation of the tetranitrile. This material underwent extensive decomposition in air at 350° over 24 hours.

Three attempts also were made to prepare a polymeric metal-free phthalocyanine by the cocondensation of phthalonitrile and 3,3′,4,4′-tetracyanodiphenyl ether with sodium amylate in amyl alcohol. Purification was less satisfactory and analytical data less meaningful, since there is no element whose content is as sensitive to structure as is copper. However, viscosities in pyridine ranged from 0.07 to 0.28, while the monomeric metal-free phthalocyanine had a viscosity of 0.10. Thus, it appears that no high molecular weight materials were formed. These materials also underwent extensive decomposition at 350° in air over 24 hours.

Acknowledgment.—We are indebted to Mr. Jozsef Nemeth, Miss Claire Higham and Mrs. Ruby Ju of the Microanalytical Laboratory of the University of Illinois; to Clark Microanalytical Laboratory, Urbana, Ill., for the microanalyses, and to Mr. Paul McMahon of the University of Illinois for the infrared data.

Experimental

4-Bromo-*o*-xylene, n^{18}D 1.5581 (lit. n^{22}D 1.5558), was prepared in 92% yield according to the method of Wesansky and Ansbacher[8] by the direct bromination of *o*-xylene.

3,3′,4,4′-Tetramethyldiphenyl Ether, m.p. 58–59°, was prepared in 61% yield from 4-bromo-*o*-xylene and 3,4-dimethylphenol by the method of Marvel and Rassweiler.[6]

3,3′,4,4′-Tetracarboxydiphenyl Ether, m.p. 215–217° dec., was prepared in 72% yield (lit. 25%) by the potassium permanganate oxidation of 3,3′,4,4′-tetramethyldiphenyl ether by a modification of the method of Marvel and Rassweiler.[6] The product was isolated from the acidified reaction mixture by exhaustive ether extraction rather than filtration.

3,3′,4,4′-Tetracarbonamidodiphenyl Ether.—To a slurry of 227 g. (0.665 mole) of 3,3′,4,4′-tetracarboxydiphenyl ether in 1500 ml. of water was added, with stirring, 745 ml. of concentrated ammonia. Excess ammonia was removed by bubbling nitrogen through the solution at 65°. The solution then was filtered and concentrated nearly to dryness. The paste now was heated at 250–280° until ammonia evolution ceased. The infrared spectrum (Nujol mull) of the crude product had bands at 3150 cm.$^{-1}$ (N–H str.) and 1768 and 1706 cm.$^{-1}$ (carbonyl of cyclic imide). A sample of this diimide was sublimed for analysis. The sample did not melt below 300°.

Anal. Calcd. for $C_{16}H_8N_2O_5$: C, 62.34; H, 2.62; N, 9.09. Found: C, 62.31; H, 2.73; N, 9.14.

To the crude diimide was added 750 ml. of concentrated ammonia, and the slurry was stirred at room temperature for 20 hours. The mixture was filtered, and the solid was reslurried with concentrated ammonia, refiltered, and the filter pack was washed with concentrated ammonia and finally water. The product was dried to constant weight at reduced pressure over calcium chloride. The yield was 192 g. (84.5% based on acid). The infrared spectrum (Nujol mull) had bands at 3400 and 3290 cm.$^{-1}$ (N–H str.) and 1665 and 1625 cm.$^{-1}$ (carbonyl of primary imide). Due to the extreme insolubility of this material, analytical purity was not achieved.

Anal. Calcd. for $C_{16}H_{14}N_4O_5$: C, 56.13; H, 4.14. Found: C, 55.67; H, 4.20.

3,3′,4,4′-Tetracyanodiphenyl Ether.—To 184.5 g. (0.54 mole) of 3,3′,4,4′-tetracarbonamidodiphenyl ether in 1 liter of dimethylformamide was added at a rapid rate 219 ml. (369 g., 3.1 moles) of thionyl chloride. The temperature rose to 80°, then was allowed to drop to 50°. After 2.25 hours at 50°, an additional 123 ml. (206 g., 1.7 moles) of thionyl chloride was added, and the temperature was maintained at 58° for 5.75 hours. The mixture then was poured onto 3.5 liters of crushed ice, and the cold mixture was filtered. The filter cake was washed with cold water, suspended in 5% sodium hydroxide, filtered and washed, and the process was repeated. This process removed any imide side products. The product then was washed with water until the washings were nearly neutral, and dried at reduced pressure over phosphoric anhydride. The yield was 117 g. (80%). Further purification was achieved by dissolving the product in dimethylformamide, treating with decolorizing charcoal, and triturating with water. The product next was recrystallized once from acetonitrile–dimethylformamide–water, ten times from dimethylformamide–water, and twice from acetone. A sample of this material gave an analysis consistent with the tetranitrile and $^1/_4$ mole of water of crystallization; it began to turn light green at 243° and melted to a blue-green liquid at 254–256° (this property is typical of aromatic *o*-dinitriles). The infrared spectrum (Nujol mull) had a band at 2238 cm.$^{-1}$ (C–N str.), and there was no absorption in the carbonyl region. A sample was sublimed for analysis, m.p. 255°.

Anal. Calcd. for $C_{16}H_6N_4O$: C, 71.10; H, 2.24. Found: C, 70.53; H, 2.39.

Cocondensation of Phthalonitrile and 3,3′,4,4′-Tetracyanodiphenyl Ether with Copper-bronze.—The phthalonitrile, 3,3′,4,4′-tetracyanodiphenyl ether and copper-bronze were ground intimately together, then transferred to the reaction vessel, a large test-tube for numbers 1–8, 11 and 12, and a sealed tube for number 10. The quantities of reactants used appear in Table IV. Each mixture was then heated at 275°. It was frequently necessary to scrape the sides of the test-tube to remove sublimed phthalonitrile. The dark melt gradually thickened and became a hard solid. After cooling, the product was ground with hot acetone, filtered, and dried at 125°. The polymer so prepared was added to 50 ml. of concentrated sulfuric acid, and shaken for 20 hours at room temperature, then filtered through a coarse sintered-glass funnel. The filtrate and residue were then added to ice-water. After standing for several hours, the mixture was centrifuged, the supernate was decanted, and the precipitate was collected on a büchner funnel after being slurried with 95% ethanol.

A portion of sample 5 was heated at 280–300° in a test-tube for five hours and then purified in the manner described above. One-half gram of the cold sulfuric acid-soluble fraction of sample 11 was fused for 20 minutes at 300° with 0.055 g. (0.00051 mole) of *m*-phenylenediamine. The product was washed with hot ethanol and acetone. It was completely insoluble in sulfuric acid.

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(8) W. A. Wesansky and S. Ansbacher, *Org. Syntheses*, **28**, 22 (1948).

TABLE IV

CONDITIONS FOR COCONDENSATION REACTIONS WITH COPPER-BRONZE

No.	Phthalonitrile g.	mole	Tetranitrile g.	mole	Copper-bronze g.	g. atoms	Dinitrile/ tetranitrile	Reacn. time, hr.	Product, g.	Yield, %
1	0.946	0.0074	2.000	0.0074	0.311	0.0049	1.00/1.00	3	1.5	47
2	1.421	.0111	2.000	.0074	.394	.0062	1.50/1.00	3	1.9	50
3	1.800	.0141	2.000	.0074	.457	.0072	1.90/1.00	3	2.2	51
4	1.890	.0148	2.000	.0074	.470	.0074	2.00/1.00	3	2.4	55
5	1.988	.0155	2.000	.0074	.482	.0076	2.10/1.00	3	2.9	65
6	2.080	.0163	2.000	.0074	.502	.0079	2.20/1.00	3	2.4	52
7	2.364	.0185	2.000	.0074	.546	.0086	2.50/1.00	3	2.6	53
8	2.710	.0222	2.000	.0074	.629	.0099	3.00/1.00	3	3.7	69
10	1.988	.0155	2.000	.0074	.482	.0076	2.10/1.00	11.25	2.5	56
11	...	....	2.000	.0074	.236	.0037	....	3	1.6	71
12	...	....	3.000	.0111	.356	.0056	....	11.25	2.5	75

TABLE V

CONDITIONS FOR COCONDENSATION WITH SODIUM AMYLATE

No.	Phthalonitrile g.	mole	Tetranitrile g.	mole	Sodium g.	g. atoms	Dinitrile/ tetranitrile	Yield, %	$\eta^{a\ b}$	(g./100 ml.)
13	1.988	0.0155	2.000	0.0074	0.697	0.6303	2.10/1.00	50	0.28	(0.27)
14	1.890	.0144	2.000	.0074	.680	.0296	2.00/1.00	65	.19	(.13)
15	1.813	.0141	2.000	.0074	.664	.0289	1.90/1.00	55	.07	(.44)

[a] Viscosities in pyridine at 25°. [b] Viscosity of monomeric metal-free phthalocyanine is 0.10 (0.25 g./100 ml.).

Cocondensation of Phthalonitrile and 3,3',4,4'-Tetracyanodiphenyl Ether with Sodium Amylate.—To a solution of sodium amylate in 32 ml. of amyl alcohol was added an intimate mixture of phthalonitrile and 3,3',4,4'-tetracyanodiphenyl ether. After refluxing for 40 minutes, 50 ml. of methanol was added, and the mixture allowed to stand for two hours at room temperature. The product was collected on a büchner funnel, washed with hot methanol until the washings were colorless and then extracted for three days with acetone in a Soxhlet extractor. Reaction conditions and viscosities appear in Table V.

Heat stabilities in air were determined by placing about 10 mg. of sample in a fusion tube, and placing the tube in an oven at the desired temperature. The tube then was weighed periodically to check weight loss.

URBANA, ILL.

[CONTRIBUTION FROM THE ROCKEFELLER INSTITUTE]

Isolation and Structure of the C_{16} Unsaturated Fatty Acids in Menhaden Body Oil[1]

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A mixture of C_{16} unsaturated fatty acids was isolated from menhaden body oil by fractional crystallization, followed by high vacuum fractional distillation. Countercurrent distribution yielded pure tetraene, triene, diene and monoene fractions. The structures of these acids were determined by oxidative and reductive ozonolysis with identification of the fragments by reversed phase, paper and gas–liquid chromatographic analysis. These several acids were identified: *n*-hexadeca-6,9,12,15-tetraenoic acid, *n*-hexadeca-4,7,10,13-tetraenoic acid, *n*-hexadeca-6,9,12-trienoic acid, *n*-hexadeca-7,10,13-trienoic acid, *n*-hexadeca-6,9-dienoic acid, *n*-hexadeca-9,12-dienoic acid, *n*-hexadeca-9-monoenoic acid and *n*-hexadeca-8-monoenoic acid. Gas–liquid chromatographic characteristics of these acids are described.

In recent years a number of polyenoic fatty acids with chain lengths C_{18}, C_{20} and C_{22} have been isolated from natural sources in the laboratories of Klenk,[2–8] Riemenschneider[9] and Lundberg.[10] Structural studies of these acids suggest certain common pathways in their biosynthesis, for in widely diverse systems (triglycerides and phosphatides of liver and brain in marine and mammalian species) the polyenoic acids have two characteristics in common: (1) the double bonds are arranged in the divinyl-methane rhythm, often called methylene-interrupted or "skipped" double bonds, and (2) each of these acids belongs either to the linoleic or to the linolenic acid family, *i.e.*, with the double bond farthest from the carboxyl group six or three carbons from the terminal methyl group, respectively.

Studies of the C_{16} unsaturated acids have been much less comprehensive. Smith and Brown[11] in 1945 were the first to note the presence of a C_{16} tetraene as a component in menhaden oil and in 1958 Mangold and Schlenk[12] confirmed the presence in menhaden oil of C_{16} mono-, di-, tri- and tetraenes. A C_{16} tetraene also was noted by Paschke

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