[Contribution from The B. F. Goodrich Research Center]

The Structure of the Compound $C_{11}H_6N_6$ Prepared from Malononitrile and Formaldehyde

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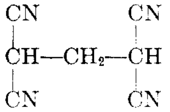
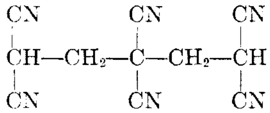
Condensation of malononitrile and formaldehyde gives 1,1,3,3-tetracyanopropane and a compound of the composition $C_{11}H_6N_6$ for which the structure 1,1,3,3,5,5-hexacyanopentane is given in the original literature. The chemical and physical properties of the compound $C_{11}H_6N_6$ are discussed and a new structure, 2,2,4,4,6-pentacyanocyclohexanonimine, is proposed.

In 1922 O. Diels and co-workers[1] reported the preparation of a solid of m.p. 136–137° having the composition $C_7H_4N_4$. This solid, which was prepared by the base-catalyzed condensation of malononitrile and formaldehyde, was assigned structure I. Diels and Conn,[2] subsequently reported the preparation of a second compound from the base-catalyzed condensation of malononitrile and formaldehyde. This compound having m.p. 226° and the composition $C_{11}H_6N_6$ was assigned structure II. Considerable work in this laboratory indicates that the solid of composition $C_{11}H_6N_6$ does not have structure II. A new structure for this substance is proposed and the chemical and physical properties of the compound $C_{11}H_6N_6$ are presented.



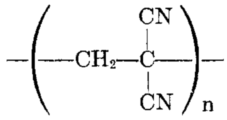
$(NC)_2CH-CH_2-CH(CN)_2$

I



$(NC)_2CH-CH_2-C(CN)_2-CH_2-CH(CN)_2$

II



$-\left(-CH_2-C(CN)_2-\right)_n-$

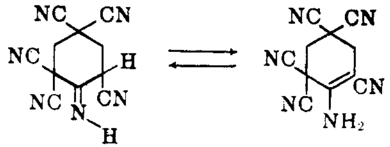
IV

When I is heated at 150 to 200° it decomposes to give vinylidene cyanide (III) and malononitrile.[3] When polyvinylidene cyanide (IV) is heated above 160° it depolymerizes to give III.[4] However, when the compound $C_{11}H_6N_6$ is heated under conditions which give III from I and IV, no III is produced.[5]

The infrared absorption spectrum of the compound $C_{11}H_6N_6$ was determined as a mull in Nujol (25—7.5 μ) and Fluorlube (7.5–2 μ). The spectrum is not consistent with structure II. Although absorption peaks due to $C\equiv N$, C—C, and C—H are present, three peaks at 2.92, 2.98, and 3.09 μ due to N—H, a peak at 6.06 μ due either to $C=N$ or $C=C$, and a peak at 6.13 μ due to NH_2 are also present. That the peaks near 3 μ are due to N—H and that the peak at 6.13 μ is due to NH_2 was shown by treating $C_{11}H_6N_6$ in acetonitrile with deuterium oxide. The deuterated solid had N—H peaks of lower intensity and N—D peaks at 3.88, 3.92, 3.99, 4.10, and 4.14 μ. The peak at 6.13 μ due to NH_2 disappeared in the deuterated compound. In the region from 7.5 μ to 10 μ numerous sharp peaks were present. These are believed to be due to ring vibrations and suggest that $C_{11}H_6N_6$ is a cyclic compound. The infrared spectrum of pure I contains no peaks attributable to N—H, $C=C$ $C=N$, NH_2, or rings.[6]

The molecular weight of a compound $C_{11}H_6N_6$ is 222.21. Diels and Conn[2] found values of 158.8 and 162.7 by the elevation of the boiling point of acetone. These values were reconciled with the theoretical value by assuming structure II, decomposition of II at the boiling point of acetone to give III (and I), and polymerization of III to a high polymer. The experimental values then were multiplied by 3/2 to give the values 238.2 and 243.9. Since $C_{11}H_6N_6$ is now known not to decompose to give III, the molecular weight was investigated. Ebullioscopic determinations in various solvents gave the following results: Acetone, 162, 170, 174 in agreement with Diels and Conn;[2] Acetonitrile, 177 and 179; Dioxane, 233. Cryoscopic determinations in dioxane gave 217, 216, and 215.

From the previous discussion it is evident that the compound $C_{11}H_6N_6$ does not have structure II. The experimental facts appear consistent with structure V[7] and its tautomeric form VI. Structure V can be derived from structure II by cyclization. Since V contains a tertiary hydrogen atom which can ionize in a basic solvent and V and VI contain respectively an imino and an amino group capable of accepting a proton from an acidic solvent, the



V VI

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[1] Diels, Gartner, and Kaack, *Ber.*, **55**, 3439 (1922).

[2] Diels and Conn, *Ber.*, **56**, 2076 (1923).

[3] Ardis, *et al.*, *J. Am. Chem. Soc.*, **72**, 1305 (1950).

[4] Ardis and Gilbert, U. S. Patent 2,535,827 (Dec. 26, 1950); *Chem. Abstr.*, **45**, 3196[b] (1951).

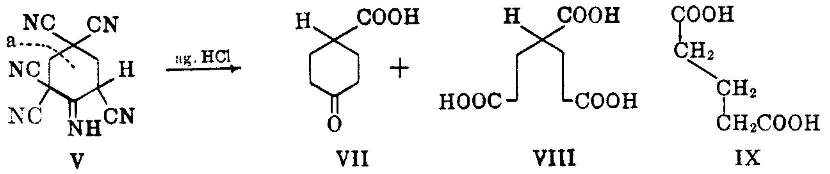
[5] This work was carried out by H. Gilbert.

[6] The deuteration experiment was carried out by J. J. Shipman. Infrared spectra were determined and interpreted by J. J. Shipman, J. P. Kiehl, and A. Hawthorne.

[7] This structure was suggested by H. J. Heller.

anomalous molecular weight results obtained in certain solvents may be due to such interaction with the solvent.

Hydrolysis of the compound $C_{11}H_6N_6$ and conventional isolation of products was shown to produce γ-carboxypimelic acid and a small amount of glutaric acid.[8] Hydrolysis of a compound having structure V was expected to proceed as follows.



V VII VIII IX

Partial hydrolysis of V would give a large number of intermediate β-keto acids or β-keto acid derivatives which on complete hydrolysis and decarboxylation would give VII. Hydrolytic ring opening of V or of any of the intermediate hydrolysis products would give VIII and IX. Hydrolytic cleavage of the type indicated at "a" (V) was observed in the degradation of IV[9] and in the hydrolysis of 1,1,3,3,5,5-hexacarbethoxypentane.[10]

The mixture of non-volatile acids produced in the hydrolysis of V was shown by circular paper chromatography to consist of VII, VIII, IX, and three unidentified acids. Based on the size of the spots in chromatograms of the total non-volatile acids formed in the hydrolysis, the acids in order of abundance were VIII > > IX > VII. VII was estimated to comprise less than 1% of the acid mixture. The unidentified acids were present in amounts comparable to VII. The presence of VII was confirmed by preparing the 2,4-dinitrophenylhydrazone and comparing it with authentic 2,4-dinitrophenylhydrazone of VII. VII was not formed by cyclization of VIII during the hydrolysis of V, as shown by subjecting VIII to the same conditions of hydrolysis and isolation as V. No VII was detected in the recovered acid.

The evidence presented clearly shows that the compound $C_{11}H_6N_6$ does not have structure II. The proposed structures V and VI appear to be consistent with the known properties of the compound.

EXPERIMENTAL[11]

2,2,4,4,6-Pentacyanocyclohexanonimine (V). V was prepared by the procedure of Diels and Conn.[2] The crude, nearly colorless V darkened above 200° and had m.p. 231–234° (melt nearly black). Introduction of the capillary tube into the bath at 220° gave m.p. 233–235° (melt dark brown). Colorless V could be obtained with considerable loss by dissolving V rapidly in boiling distilled water, stirring briefly with decolorizing carbon, filtering rapidly with suction (filter-aid), and cooling rapidly in an ice-bath. Colorless V was more easily obtained by acidifying the distilled water used in the recrystallization to *ca.* *p*H 3 with dilute sulfuric acid. Colorless V darkened above 200° and had m.p. 238–239° (brown melt). Introduction of the capillary into the bath at 220° gave m.p. 238–240° (yellow melt). The melting points are not accurately reproducible since they depend on heating rate.

Anal. Calc'd for $C_{11}H_6N_6$: C, 59.45; H, 2.72; N, 37.83. Found: C, 59.29, 59.18; H, 2.77, 2.79; N, 37.88, 37.86.

Chromatography. Whatman No. 2 filter paper circles (24 cm.) were washed as described by Kennedy and Barker[12] and the papers were marked and the solutions were applied as described by Airan, *et al.*[13] Developer 1 was prepared by mixing 15 ml. of distilled water, 85 ml. of commercial absolute ethanol, and 1 ml. of 28% aqueous ammonia. Developer 2 was prepared using 25 ml. of distilled water, 75 ml. of commercial absolute ethanol, and 1 ml. of 28% aqueous ammonia. Development was stopped when the solvent front was *ca.* 5 mm. from the edge of the paper (5 to 6 hours). After drying in air at room temperature for 30 minutes the papers were sprayed with the bromophenol solutions of Kennedy and Barker.[12] The papers were dried briefly and the location of the solvent front was marked and the spots were outlined.

Hydrolysis of V. When a suspension of 17.18 g. (0.077 mole) of V in 85 ml. of distilled water and 85 ml. (1.02 moles) of conc'd hydrochloric acid was heated to boiling, V rapidly dissolved and gas evolution began. After refluxing for 24 hours the colorless solution was freed of water and hydrogen chloride *in vacuo* to leave a solid residue. Extraction of the residue with eight portions of boiling ether (total volume, 220 ml.) left a residue of ammonium chloride. The ether extract was dried with magnesium sulfate, filtered, and freed of ether *in vacuo* to leave 11.75 g. of colorless solid acid. The solid was extracted with two 20-ml. portions of chloroform and the insoluble acid was washed on a suction filter with a further 5 ml. of chloroform. The filter cake was dried to give 11.11 g. (68.4%) of crude VIII of m.p. 102.5–111°. One recrystallization from acetone-chloroform gave 8.47 g. (57.2%) of VIII of m.p. 111–113.5°. Reported melting points of VIII are 113–114.5°[10] and 114°.[14] The chloroform filtrate was freed of chloroform *in vacuo* to leave 0.37 g. of partly crystalline acid mixture. This acid mixture was converted to a solution of its ammonium salts and chromatographed using developer 1 to give four well separated arcs and a spot which hardly moved from the origin. The average R_f values together with standard deviations for the four arcs were 0.32 (0.02), 0.46 (0.02), 0.58 (0.03), and 0.75 (0.00). Authentic glutaric acid (IX) had R_f 0.31 (0.01). Authentic VII, prepared by acetic anhydride cyclization and purified through the semicarbazone,[15] had R_f 0.60 (0.01).

When the mixture was chromatographed using developer 2, six arcs with the following R_f values were obtained: 0.23 (0.01), 0.40 (0.00), 0.53 (0.01), 0.65 (0.02), 0.71 (0.01), 0.80 (0.01). Authentic VIII of m.p. 114.5–115°, prepared

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[8] This work was carried out by H. J. Heller.

[9] Gilbert, *et al.*, *J. Am. Chem. Soc.*, **76**, 1074 (1954).

[10] Bottomley and Perkin, Jr., *J. Chem. Soc.*, **77**, 300 (1900).

[11] All melting points are uncorrected.

[12] Kennedy and Barker, *Anal. Chem.*, **23**, 1033 (1951).

[13] Airan, *et al.*, *Anal. Chem.*, **25**, 659 (1953).

[14] Enkvist, *Soc. Sci. Fennica, Commentations Phys.-Math.*, **9**, No. 11 [*Chem. Abstr.*, **32**, 6624^7 (1938)].

[15] Perkin, Jr., *J. Chem. Soc.*, **85**, 424 (1904).

by hydrolysis of γ,γ-dicarbethoxypimelonitrile,[16] had R_f 0.41 (0.01). Authentic VII had R_f 0.73 (0.03).

Treatment of an aqueous solution of the chloroform-soluble acids with an excess of 2,4-dinitrophenylhydrazine reagent[17] gave a crude 2,4-dinitrophenylhydrazone of m.p. 185–187.5°. When a solution of authentic VII was similarly treated, the crude 2,4-dinitrophenylhydrazone of VII had m.p. 186–187.5°. Aqueous solutions of the ammonium salts of the two derivatives were chromatographed using developer 1. No indicator spray was used. The 2,4-dinitrophenylhydrazone prepared from the chloroform-soluble acid gave two arcs having R_f values of 0.64 and 0.90 (weak). The 2,4-dinitrophenylhydrazone of VII had R_f 0.64 (0.01).

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(16) Bruson and Riener, *J. Am. Chem. Soc.*, **65**, 23 (1943).

(17) Shriner and Fuson, *The Systematic Identification of Organic Compounds*, 3rd Edition, John Wiley and Sons, Inc., New York, 1948, p. 97.