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ATTEMPTED SYNTHESIS OF 1,2,7,8-PYRENETETRAMINE

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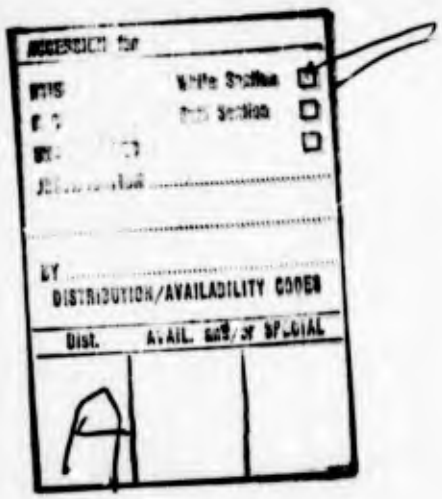

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An attempt was made to prepare 1,2,7,8-pyrenetetramine to be used as a monomer in the development of a high temperature polyquinoxaline polymer

Unfortunately, the monomer was too unstable for purification. The characterization of the monomer was accomplished by the preparation of a derivative, 1,2,7,8-pyrenetetracetamide, by two alternate routes.

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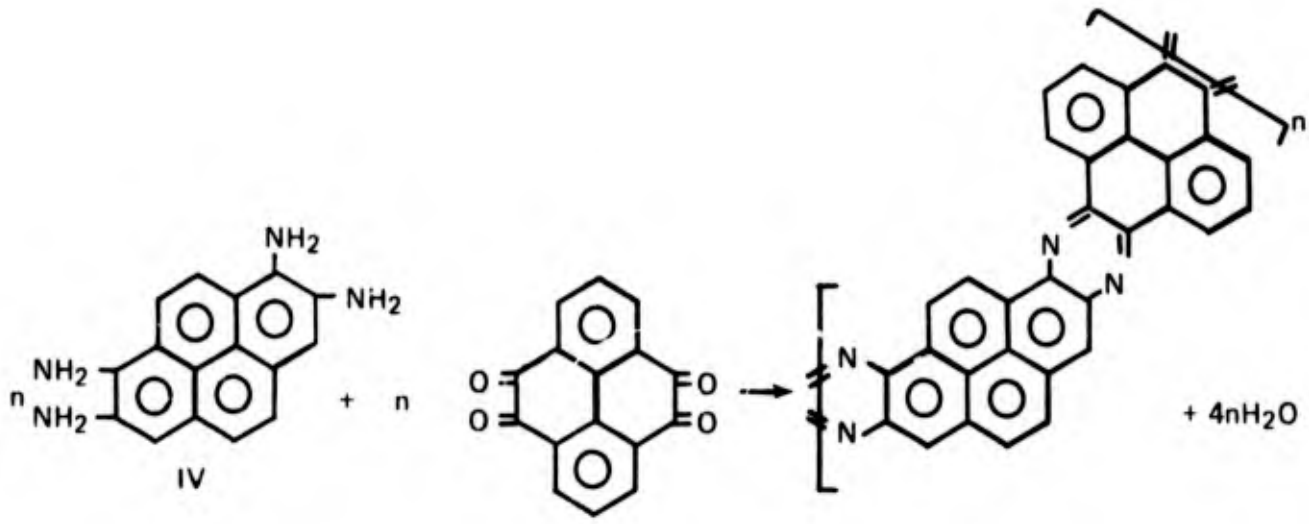
INTRODUCTION

Polyquinoxaline ladder polymers have unusual thermal stability.[1] This outstanding thermal behavior is accounted for by the nonlinear arrangement of the fused aromatic rings.

In accordance with our interest in organic polymers of high thermal stability we felt it worthwhile to attempt to prepare 1,2,7,8-pyrenetetramine (IV) in order to conduct condensation polymerizations with 4,5,9,10-pyrenetetrone. Since this polyquinoxaline polymer would be composed entirely of fused rings, it would be totally ladder, and capable of existing in syn and anti configurations. The expectation is that this polymer would have reasonable solubility in addition to high temperature resistance.

In order to prepare this new polymer the previously unknown tetramine IV had to be synthesized. In this report we will discuss the synthesis and properties of the tetramine IV and its derivatives.



EXPERIMENTAL

Infrared spectra were run on a Perkin-Elmer Model 137 Spectrophotometer. Elemental analyses were determined by the Galbraith Laboratories, Inc. Compound I was found to be pure by a thermal analyzer, DuPont Instrument Model 990. Molecular weight determinations were conducted in dimethylacetamide on a Perkin-Elmer Vapor Phase Molecular Weight Apparatus Model 115.

1,8-Pyrendiacetamide (I)

1,8-pyrenediamine (30 g, 0.129 mole) and 300 ml of glacial acetic acid were heated to 90 C with vigorous stirring. Acetic anhydride (60 ml, 0.63 mole) was added drop-wise within 0.5 hr. The reaction mixture was maintained at 90 C for

1. FRAZER, A. H. *High Temperature Resistant Polymers.* Interscience Publishers, A Division of John Wiley & Sons, 1968, p. 192-197.

1 hour and then cooled, after which it was poured on ice and filtered. The product was thoroughly washed with water and once with ethanol. Several washings with hot benzene insured the removal of any starting material. The product was dried; 40.8 g (99.4%).

Calcd. for: ($C_{20}H_{16}N_2O_2$); C, 75.93; H, 5.10; N, 8.86%.

Found: C, 75.66; H, 5.01; N, 8.63%.

The infrared spectrum is consistent with the structure of the compound.

2,7-Dinitro-1,8-Pyrenediacetamide (II)

To 1,8-pyrenediacetamide (I) (5 g, 0.58 mole) in 80 ml of glacial acetic acid was added, within 20 minutes, 2.50 ml of concentrated nitric acid diluted in 20 ml of glacial acetic acid. The reaction mixture was heated to 100 C and maintained at that temperature for 20 minutes and then quickly cooled to room temperature. The orange solids were filtered, washed with water and methanol. The orange mixture was dissolved in hot dimethylacetamide and slowly forced out of solution by the addition of methanol. The product was filtered and washed thoroughly with methanol and dried; 3.21 g (50%).

Calcd. for: ($C_{20}H_{14}N_4O_6$); C, 59.11; H, 3.47; N, 13.79%; Mol. Wt., 406.

Found: C, 58.70; H, 3.57; N, 13.48%; Mol. Wt., 412.

The infrared spectrum is consistent for the assigned structure.

2,7-Dinitro-1,8-Pyrenediamine (III)

To a slurry of compound II (0.488 g, 0.0012 mole) in 30 ml of methanol was added a solution of 3.5 g of potassium hydroxide in 10 ml of methanol. The color changed from orange to brick red. After heating at reflux for three hours, the reaction mixture was cooled to ambient temperature and filtered. The crude product was washed with water and dried; 0.318 g (84%). The dark red product was dissolved in dimethylacetamide and filtered. The filtrate was poured into water to precipitate a dark red solid which was filtered and washed with water and air dried to provide 0.25 g (66%) of 2,7-dinitro-1,8-pyrenediamine (III).

Calcd. for: ($C_{16}H_{10}N_4O_4$); C, 59.63; H, 3.13; N, 17.39%.

Found: C, 59.91; H, 3.36; N, 16.42%.

The infrared spectrum is consistent for the assigned structure.

Preparation of 1,2,7,8-Pyrenetetramine (IV)

To a solution of sodium sulfide nonahydrate (34.5 g 0.143 mole) dissolved in 55 ml of water and 35 ml of ethanol, was added compound III (5 g, 0.0155 mole). The reaction mixture was heated at reflux for 2.5 hour. The crude product was filtered, washed with water and air dried; 1.92 g (47%). The brown solid was acetylated directly to avoid decomposition.

Acetylation of 1,2,7,8-Pyrenetetramine (IV)

The above reduction product (1.92 g) was heated at 85 C for two hours in 50 ml of glacial acetic acid and 10 ml of acetic anhydride, and then cooled to room temperature. An addition of 200 ml of water, to the reaction mixture resulted in precipitation. The solid material was filtered and thoroughly washed with water. The product was also washed with acetone and chloroform, and dried in vacuo to provide what we believe to be 1,2,7,8-pyrenetetracetamide (V); 2.2 g (70%).

Calcd. for: ($C_{24}H_{22}N_4O_4$); C, 66.96; H, 5.15; N, 13.02%.

Found: C, 65.58; H, 4.63; N, 12.51%.

The infrared spectrum is consistent for the assigned structure.

Preparation of 2,7-Diamino-1,8-Pyrenediacetamide (VI)

The 2,7-dinitro-1,8-pyrenediacetamide (II) (5 g, 0.0158 mole) was added to 36 g of sodium sulfide nonahydrate dissolved in 50 ml of water and 50 ml of ethanol and then heated at reflux for three hours. After cooling to room temperature, the mixture was filtered. The deep green product was washed thoroughly with water and dried in vacuo; 2.2 g (52%). No further purification of the material was conducted prior to elemental analysis.

Calcd. for: ($C_{20}H_{18}N_4O_2$); C, 69.35; H, 5.24; N, 16.18%; Mol. Wt., 346.

Found: C, 70.00; H, 5.02; N, 15.53%; Mol. Wt., 328.

The infrared spectrum is consistent for the assigned structure.

Acetylation of 2,7-Diamino-1,8-Pyrenediacetamide (VI)

To a slurry of compound VI (1.3 g, 0.00375 mole) in 40 ml of anhydrous pyridine, cooled to 10 C, was added, drop-wise, 5 ml of acetyl chloride. The mixture was stirred for 30 minutes and then poured into 50 ml of 3N hydrochloric acid and ice. The green solid was filtered, washed with water and methanol. The resulting material was dried and yielded 1.5 (94%) of 1,2,7,8-pyrenetetracetamide (VII). For analysis, a sample was boiled in pyridine, filtered, washed with methanol and dried in vacuo.

Calcd. for: ($C_{24}H_{22}N_4O_4$): C, 66.96; H, 5.15; N, 13.02%.

Found: C, 66.02; H, 4.90; N, 12.68%.

The infrared spectra of compound V and VII are identical.

DISCUSSION

Nitration[2] of commercially available pyrene leads to two isomers; 1,6 and 1,8-dinitropyrene. The isomers are conveniently reduced by a dilute solution of

2. VOLLMAN, H., BECKER, H., CORELL, M., and STREECH, H. *Pyrene and its Derivatives.* Chem. Abs., v. 32, 1938, p 1459.

sodium sulfide in water-ethanol. The corresponding diamines are isolated by fractional crystallization. The 1,6-pyrenediamine melts at 232 to 233 C and 1,8-pyrenediamine has a melting point of 160 to 162 C.

Preparation of 1,8-Pyrenediacetamide (I)

Acetylation of 1,8-pyrenediamine with acetic anhydride produced a quantitative yield of 1,8-pyrenediacetamide (I) which was to serve as the starting material for the preparation of 1,2,7,8-pyrenetetramine (IV).

H. Vollman[2] and co-workers had prepared compound I without complete characterization. They reported that it melts at 410 C and darkens at 350 C.

Nitration of 1,8-Pyrenediacetamide (I)

Nitration of 1,8-pyrenediacetamide (I) by a mixture of nitric and acetic acids produced a mixture of mono- and dinitropyrene compounds.

It is reasonable to believe that the nitration would produce 2,7-dinitro-1,8-pyrenediacetamide (II) since acetamido radicals[3-6] are noted with regard to their strong ortho influence on substitution to aromatic ring systems.

Precipitation from dimethylacetamide-methanol solution, separated the mono and dinitro compounds and we realized 2,7-dinitro-1,8-pyrenediacetamide (II).

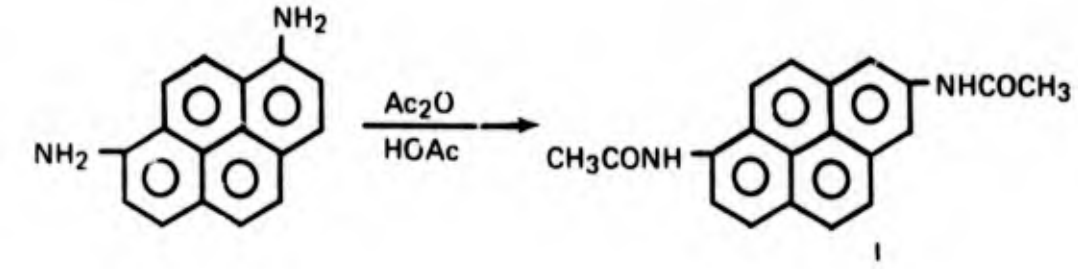
Hydrolysis of 2,7-Dinitro-1,8-Pyrenediacetamide (II)

Acetamindo radicals[5,7] are hydrolized employing acidic reaction conditions to amino derivatives. Compound II failed to achieve cleavage with sulfuric or hydrochloric acids under various reaction conditions. These observations compelled us to consider basic hydrolysis by which 2,7-dinitro-1,8-pyrenediamine (III) was obtained in good yield.

Reduction of 2,7-Dinitro-1,8-Pyrenediamine (III)

Reduction of compound III with sodium sulfide, or treatment with hydrogen and palladium, yielded a brown solid that could not be purified and appeared to be unstable in light. The solid was analyzed by infrared spectroscopy which indicated it was reduced to an amino derivative, which we consider to be 1,2,7,8-pyrenetetramine (IV).

3. NORMAN, R. O. C. *Principles of Organic Synthesis.* First Edition, Distributed in the U. S. A. by Barnes & Noble, Inc., 1968, p. 383-384.
4. BARKER, A., and BARKER, C. C. *Disubstituted Fluorenes.* J. Chem. Soc., 1954, p. 870-873.
5. BRACE, W., and MARVEL, C. S. *Polymer Containing Anthraquinone Units: Polymers from 1, 2, 5, 6-Tetraminoanthraquinone.* J. Polymer Sci., Part A-1; v. 8, 1970, p. 3177-3187.
6. GERASIMENKO, Y. E., SHIGALEVSKI, V. A., and POTELESKCHENKO, V. P. *1-Nitropyrenederivatives.* Zh. Org. Khim., v. 6, no. 11, 1970, p. 2320-2326 (Russian).
7. NAMKUNG, M. V., and FLETCHER, T. L. *Derivatives of Fluorene.* J. Org. Chem., v. 25, 1960, p. 740-744.



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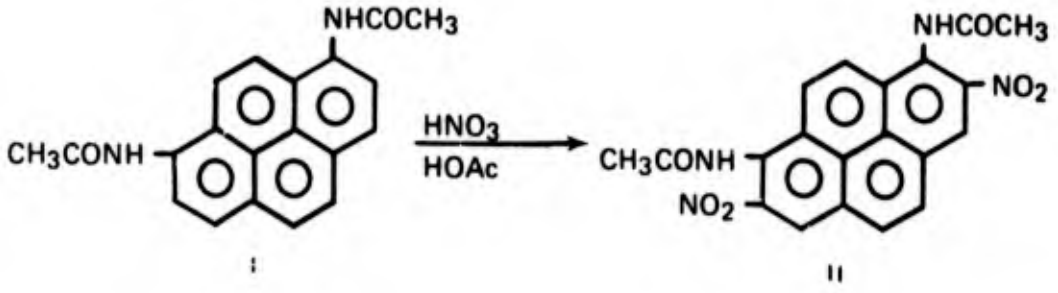

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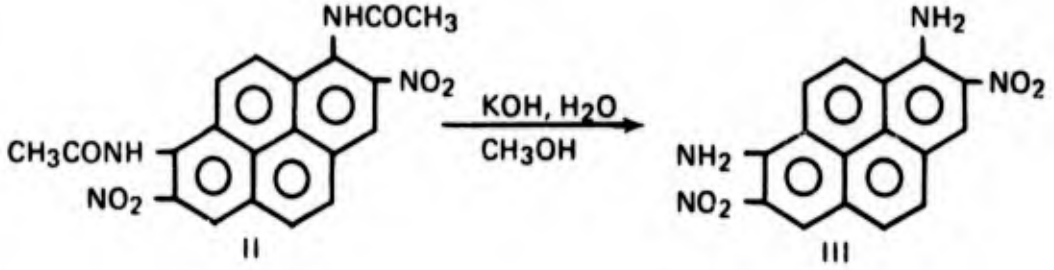


II III

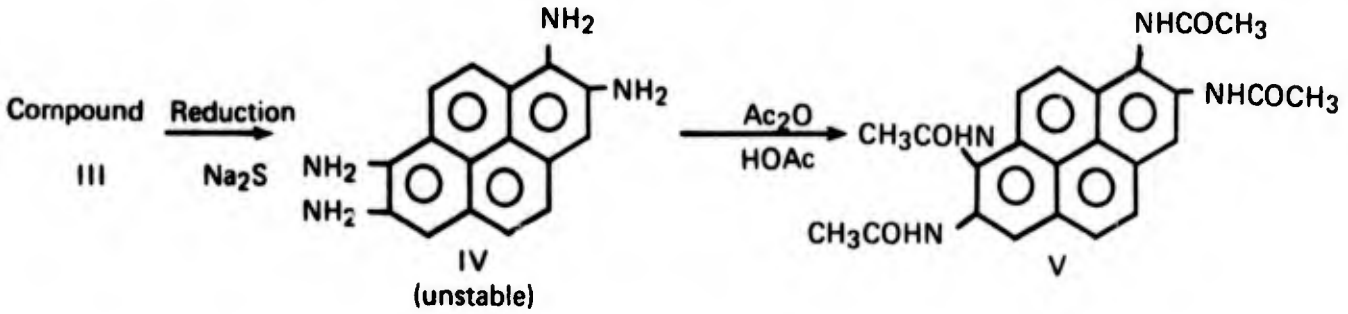
Treatment of the unstable amine IV with acetic anhydride yielded 1,2,7,8-pyrenetetracetamide (V).

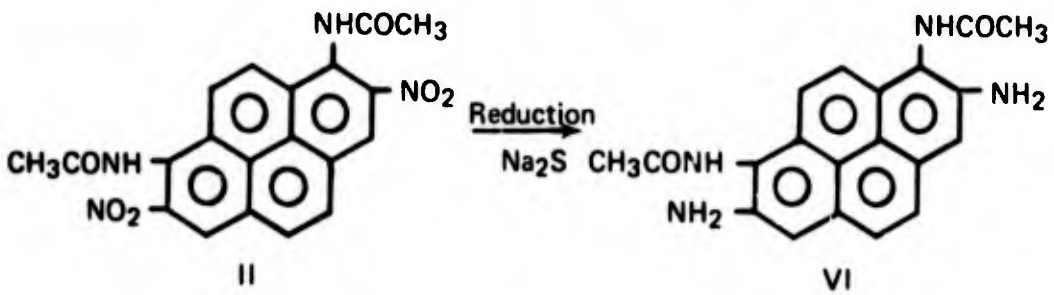
The inability to isolate compound IV was not completely unexpected, since tetraminonapthalene is too unstable to purify. Also 1,3,6,8-pyrenetetramine[8] is used in situ in a photoelectrophoresis color imaging process.

Preparation of 2,7-Diamino-1,8-Pyrenediacetamide (VI)

In order to provide an alternate route to the 1,2,7,8-pyrenetetracetamide (V), the 2,7-dinitro-1,8-pyrenediacetamide (II) was reduced with sodium sulfide to 2,7-diamino-1,8-pyrenediacetamide (VI). The reaction proceeded readily, yielding a product which was not further purified to avoid decomposition.

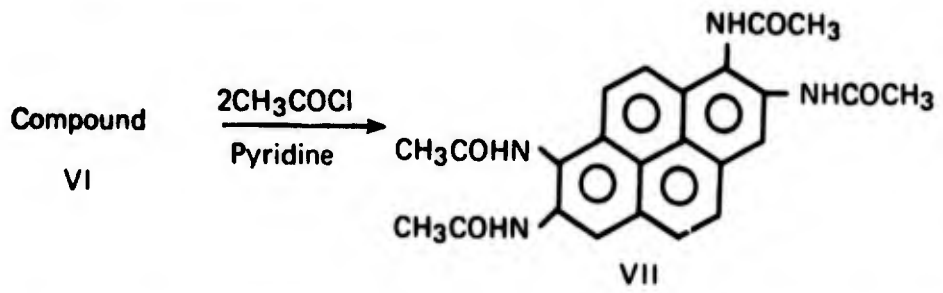
8. U. S. Patent No. 3,546,085, 8 December 1970, *Photoelectrophoretic Imaging Process and Suspension*. WEINBERGER, L., and SOLODAR, W. E., to Xerox Corp., Rochester, New York.





Treatment of 2,7-Diamino-1,8-Pyrenediacetamide (VI) with Acetyl Chloride

Reaction of compound VI with acetyl chloride yielded a product VII which is identical in all respect to 1,2,7,8-pyrenetetracetamide (V) formed by the acetylation of 1,2,7,8-pyrenetetramine (IV).



The compounds encountered in this investigation could not be crystallized and had to be precipitated out of solution; filtrations are extremely difficult because of small particle size.

An X-ray diffraction was taken on 1,2,7,8-pyrenetetracetamide (VII) to give some insight to the crystalline structure of these compounds. The X-ray pattern indicated a paracrystalline state[9] of order, possibly of the smectic type where disorders arise from errors in the hydrogen bonding pattern compared to the perfect crystal structure.

9. BONART, R. *Paracrystals*, in Encyclopedia of X-Rays and Gamma Rays, G. L. Clark, ed., New York; Reinhold, 1963, p. 686-687.

ACKNOWLEDGMENT

Dr. R. Desper ran the X-ray pattern on compound VII and explained its structure to the authors. Dr. S. Wentworth prompted the authors to report their work in pyrene chemistry and Dr. W. Davidsohn, Chief of Polymer and Chemistry Division, encouraged this research.