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Three ethynyl substituted phenylphthalimides were prepared and characterized by high pressure liquid chromatography, differential scanning calorimetry, and mass spectroscopy. When the preparation of *N*-(4-ethynylphenyl)phthalimide was attempted by the thermal cyclodehydration of *N*-(4-ethynylphenyl)-2-carboxybenzamide, *N*-(4-acetylphenyl)phthalimide was obtained as the major component. This unusual hydration of an ethynyl group was investigated and a mechanism was proposed to explain it.

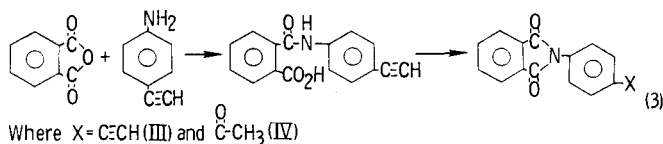
J. Heterocyclic Chem., 17, 5 (1980).

Polymers from the thermally-induced reaction of acetylene-terminated heterocyclic oligomers are under evaluation as part of a high temperature structural resin program. Our initial work involved the phenylquinoxaline (2,3) and phenyl-*as*-triazine systems (4,5). This effort has now been extended to the imide system. Acetylene-terminated imide oligomers and polymers therefrom were first reported in 1974 (6,7). One formulation of an acetylene-terminated imide oligomer is commercially available under the trade name Thermid-600® (8,9). Since this material is being evaluated as a matrix in graphite filament reinforced composites for use at temperature as high as 316°, model compound work was conducted to obtain information to serve as a guide to polymer formation. Our initial work involved the elucidation of the product from the thermally induced reaction of *N*-(3-ethynylphenyl)phthalimide (10). The work presented herein was conducted to determine the difference in properties when the ethynyl group was located in various positions on the phenylphthalimide parent compound.

The following three compounds were studied: *N*-(3-ethynylphenyl)phthalimide (I), *N*-phenyl-4-ethynylphthalimide (II), and *N*-(4-ethynylphenyl)phthalimide (III). Characterization of the various compounds is presented in Table I. Compounds I and II were prepared in near-quantitative yields as shown in Equations 1 and 2 by the following procedure. Stoichiometric quantities of the appropriate reactants were stirred at ambient temperature in glass distilled *N,N*-dimethylacetamide (DMAC, contained 0.03% water as determined by gas chromatography) for 0.5 hour followed by heating at 150° for 1 hour. The

cooled solutions were poured into water to precipitate pale yellow solids. No attempt was made to isolate the intermediate amic acid. High pressure liquid chromatography (hPLC) and mass spectroscopy verified the presence of predominantly one component in each product, the desired ethynyl *N*-phenylphthalimide.

The preparation of *N*-(4-ethynylphenyl)phthalimide was attempted under essentially identical conditions. However, instead of obtaining a quantitative yield of the desired ethynyl compound, *N*-(4-acetylphenyl)phthalimide (IV) as shown in Equation 3 was isolated as the major component. This prompted a brief investigation into the



reaction where all experiments were conducted using a stoichiometric amount of phthalic anhydride and 4-ethynylaniline. When glass distilled DMAC was used, a 78% yield of *N*-(4-acetylphenyl)phthalimide was obtained (11). This reaction was reproducible as evidenced by obtaining essentially the same yield of the acetyl compound in three separate experiments using DMAC and reactants from a common source. When dry DMAC (redistilled over calcium hydride) was used, a 77% yield of the acetyl compound was obtained with the remaining 23% identified as *N*-(4-ethynylphenyl)phthalimide. When DMAC containing 5% water was used, a 29% yield of the acetyl compound and a 71% yield of the ethynylimide were

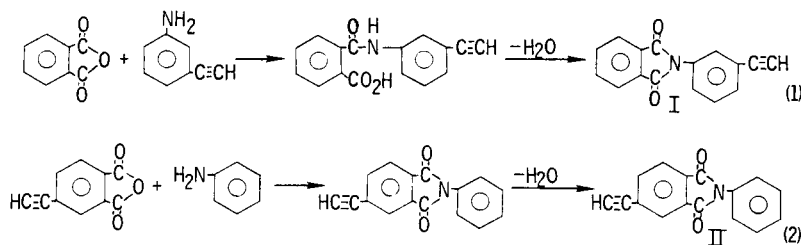


Table I

Characterization of the Compounds

Compounds	Form	M.p. °C	Formula	Mol. Wt. (1,2)	Elemental Analysis, % (2)		
					C	H	N
<i>N</i> -(3-Ethynylphenyl)-phthalimide	light tan needles	203-204	C ₁₆ H ₉ NO ₂	247 (247)	77.66 (77.72)	3.68 (3.67)	5.56 (5.67)
<i>N</i> -(4-Ethynylphenyl)-phthalimide	light yellow needles	164-165	C ₁₆ H ₉ NO ₂	247 (247)	77.81 (77.72)	3.82 (3.67)	5.62 (5.67)
<i>N</i> -Phenyl-4-ethynyl-phthalimide	light tan crystals	206-207	C ₁₆ H ₉ NO ₂	247 (247)	77.58 (77.72)	3.81 (3.67)	5.67 (5.67)
<i>N</i> -(4-Acetylphenyl)-2-carboxybenzamide	bright yellow needles	solid state dec. to imide	C ₁₆ H ₁₃ NO ₄	265 (283)	67.65 (67.84)	4.86 (4.62)	5.28 (4.95)
<i>N</i> -(4-Acetylphenyl)-phthalimide	pale yellow solid	239-240.5	C ₁₆ H ₁₁ NO ₃	265 (265)	72.31 (72.44)	4.32 (4.18)	5.41 (5.28)

(1) Determined by Mass Spectroscopy. (2) Theoretical values in parenthesis.

obtained. This was expected since the presence of excess water was expected to result in an increase in the hydration of the ethynyl group. Apparently the presence of excess water inhibits the hydration of the ethynyl group as discussed later.

N-(4-Ethynylphenyl)phthalimide was successfully prepared in quantitative yield by the chemical cyclodehydration of the precursor amic acid. A freshly prepared

DMAC solution (less than 1 hour old) of *N*-(4-ethynylphenyl)-2-carboxybenzamide was divided into two equal parts. One portion was added to a refluxing solution of acetic anhydride and pyridine which chemically cyclo-

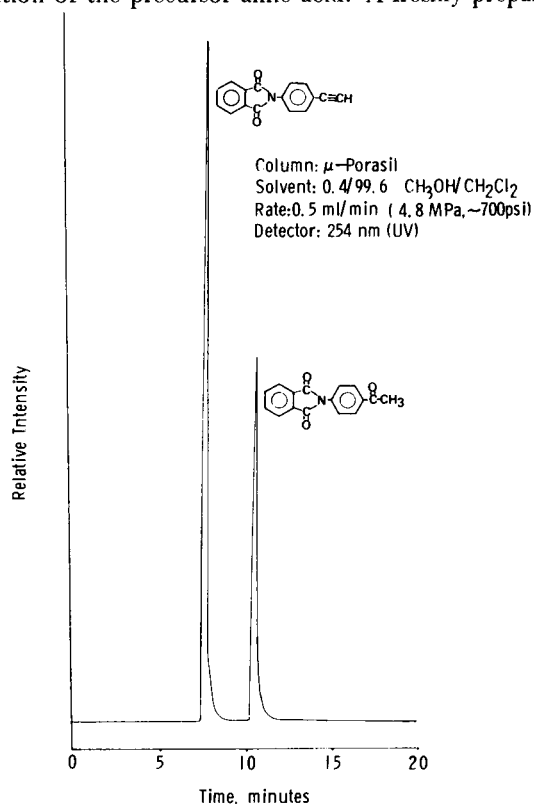


Figure 1. — High Pressure Liquid Chromatogram of Equimolar Mixture of *N*-(4-Acetylphenyl)phthalimide and *N*-(4-Ethynylphenyl)phthalimide

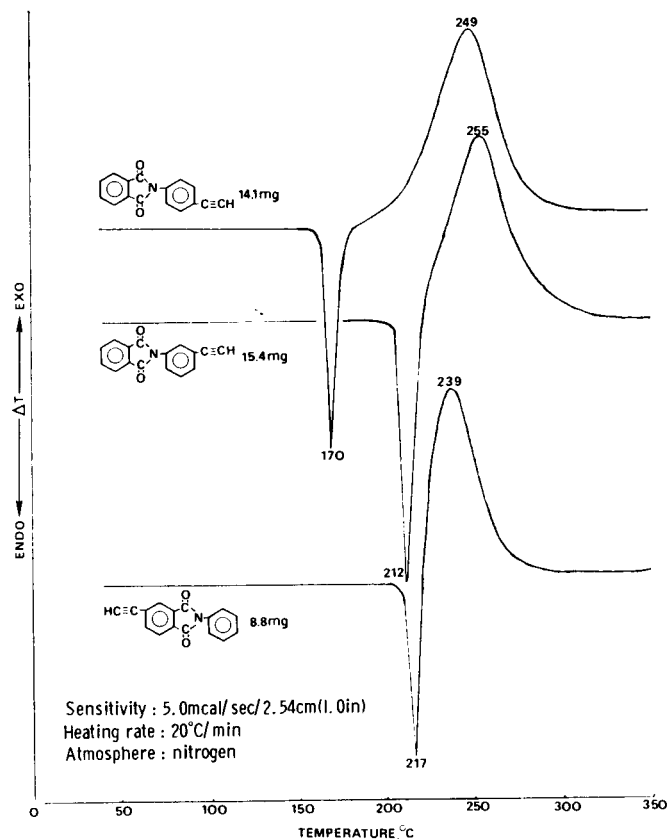


Figure 2. — Differential Scanning Calorimetric Curves of Ethynyl Phthalimides

Table II

Differential Scanning Calorimetric Data

Compound	Endothermic Peak, °C	Exothermic Peak, °C	ΔH , Kcal/mole (a)	Inflection Point after 2nd run, °C
<i>N</i> -(3-Ethynylphenyl)phthalimide	212	255	-38.6	198
<i>N</i> -(4-Ethynylphenyl)phthalimide	170	249	-37.4	210
<i>N</i> -Phenyl-4-ethynylphthalimide	217	239	-38.8	207
<i>N</i> -(4-Acetylphenyl)-2-carboxybenzamide	210 (due to imidization then 246)	394	ND	ND
<i>N</i> -(4-Acetylphenyl)phthalimide	246	395	ND	ND

(a) Heating rate of 20°/minute.

Table III

Mass Spectroscopic Data of Phthalimide Model Compounds

Compound	<i>m/e</i> (relative abundance, %)
<i>N</i> -(3-Ethynylphenyl)phthalimide	247 (93, M+), 203 (60), 104 (27), 100 (17), 76 (100), 50 (25)
<i>N</i> -(4-Ethynylphenyl)phthalimide	247 (100, M+), 203 (53), 104 (23), 100 (20), 76 (97), 50 (27)
<i>N</i> -Phenyl-4-ethynylphthalimide	247 (100, M+), 203 (75), 128 (20), 100 (53), 74 (50), 50 (25)
<i>N</i> -(4-Acetylphenyl)phthalimide	265 (30, M+), 250 (100), 222 (33), 165 (20), 104 (25), 76 (42), 50 (17)

dehydrated the amic acid to provide a quantitative yield of *N*-(4-ethynylphenyl)phthalimide. The other portion was heated to 150° for 1 hour to provide a 77% yield of *N*-(4-acetylphenyl)phthalimide and a 23% yield of *N*-(4-ethynylphenyl)phthalimide.

The stability of *N*-(4-ethynylphenyl)-2-carboxybenzamide in DMAC at ~26° was examined by characterizing samples isolated periodically over a period of 288 hours. No direct evidence of hydration of the ethynyl group was detected although some cyclodehydration of the amic acid had occurred. A small amount (~2%) of ethynylimide was found in the solution after 288 hours at 26°. The remaining portion of the aged DMAC solution of *N*-(4-ethynylphenyl)-2-carboxybenzamide was divided into two parts. One portion was refluxed in a mixture of acetic anhydride and pyridine while the other portion was heated at 150° for 1 hour. The product from the chemical cyclodehydration contained 97.9% of the ethynylimide and 2.1% of the acetylimide. Whereas, thermal conversion gave a product composed of 55% of the ethynylimide and 45% of the acetyl compound. The higher yield of the ethynylimide from the thermal conversion was surprising since an approximate 20% yield of ethynylimide was anticipated based upon previous results. No

reasonable explanation is offered to account for this unusual behavior.

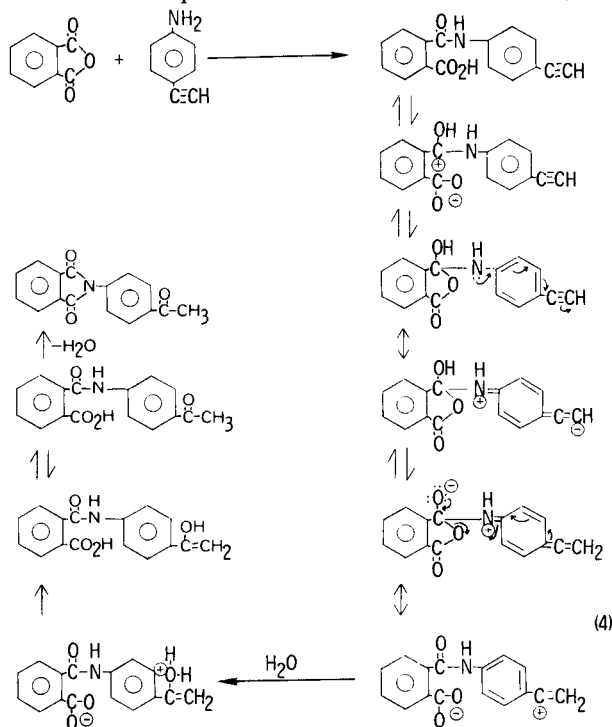
Since *N*-(4-ethynylphenyl)-2-carboxybenzamide was successfully prepared and chemically cyclodehydrated in quantitative yield to *N*-(4-ethynylphenyl)phthalimide, the hydration of the ethynyl group must occur after formation of the amic acid. Several attempts to hydrate 4-ethynylaniline in DMAC under a variety of conditions failed. In addition, during the workup of a DMAC solution of *N*-(4-ethynylphenyl)-2-carboxybenzamide which had been heated for 1 hour at 150° and subsequently quenched in water, a small quantity of yellow needles separated from the filtrate. The yellow needles were identified as *N*-(4-acetylphenyl)-2-carboxybenzamide (see Table I) which further suggested that the hydration of the ethynyl group occurred at the amic acid stage. However, some imidization of the amic acid must first occur to provide water for hydration of the ethynyl group.

A series of experiments were conducted to determine if *N*-(4-ethynylphenyl)phthalimide readily underwent hydration. Solutions of the imide in DMAC containing a small amount of water were refluxed for periods up to 24 hours. The imide was recovered unchanged. It was thought that perhaps the carboxy group in the precursor

amic acid catalyzed the hydration of the ethynyl group. Therefore, DMAC solutions of the imide containing a small amount of water and benzoic acid were refluxed for periods up to 24 hours. Again, no hydration of the ethynyl group was observed.

Of the several plausible mechanisms to explain this unusual hydration of the ethynyl group, one is proposed in Equation 4. In this mechanism, a proton is transferred from the cyclic intermediate to the polarized terminal carbon which then makes the addition of a nucleophile (water) more probable. A cyclic intermediate of this type was proposed by Bender (12) to explain the hydrolysis of phthalamic acids. The presence of excess water in DMAC is thought to inhibit the formation of the cyclic intermediate. The ethynyl group in the 4-position can partake in the proposed resonance forms whereas these are not permitted when the ethynyl group is in the 3-position. This resonance participation explains the difference in the ability of the ethynyl group in the 4-position to readily undergo hydration whereas this does not occur when the ethynyl group is in the 3-position.

The data from differential scanning calorimetric (dsc) analysis of the various compounds are presented in Table II with the dsc curves of the three ethynyl phenylphthalimides shown in Figure 2. The 4-isomer melted 42° lower than the corresponding 3-isomer which was unexpected. The heat of reaction (ΔH) for each of the three ethynyl phenylphthalimides was about the same, -38 ± 0.8 Kcal/mole. Since the trimerization of acetylene to benzene has been estimated to the -142 Kcal/mole (13), it is obvious that quantitative trimerization of the ethynyl



group of the phenylphthalimides did not occur assuming similar heats of reaction. After heating each of the ethynyl phenylphthalimides on the dsc in nitrogen at a heating rate of 20° per minute to 350°, cooling, and then rerunning the same samples at a higher sensitivity, the only thermal change detected was a baseline deflection characteristic of a second order transition. No additional thermal reaction was observed. The thermally induced reaction of *N*-(3-ethynylphenyl)phthalimide has been discussed in detail elsewhere and was shown to provide a product composed of a complex mixture of components consisting of 2 dimers, 3 trimers, 1 tetramer and higher molecular weight oligomers (10).

Mass spectroscopic data of electron impact fragmentation of the various compounds are presented in Table III. The three ethynyl phenylphthalimides exhibited very similar fragmentation patterns which involved the elimination of carbon dioxide from the imide ring to provide a fragment with an *m/e* of 203. Whereas, the fragmentation of *N*-(4-acetylphenyl)phthalimide occurred through a route which surprisingly did not involve the imide ring.

Acknowledgement.

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EXPERIMENTAL

All melting points are uncorrected. High pressure liquid chromatography was performed with a Waters Associated Model ALC 202/R401 instrument with a Model 6000 Solvent Delivery System using the indicated column and a 254 nm fixed wavelength ultraviolet detector. A Dupont Model 990 Thermal Analyzer in combination with a standard dsc cell (Dupont Catalog No. 90600-902) was used for all calorimetry measurements. The samples were hermetically sealed in Dupont supplied aluminum cups. Each sample was weighed before and after each dsc run. Essentially no change in weight was observed. The ΔH was determined by running the dsc on the time base mode at four different heating rates (5, 10, 20, and 50°/minute). The area of the transition peak was determined by drawing a line from the point where the thermogram departed from the baseline to the point where it returned. This enclosed area was measured with a planimeter.

A Finnigan Model 3300 Quadrupole Mass Spectrometer equipped with a Model 6000 Data System was used to obtain the electron-impact spectra of each compound. Samples were introduced into the ion source with a programmable temperature solid inlet probe. Each spectra was obtained by heating the sample at 2°/minute from the ion source temperature (100°) to a temperature where enough sample was vaporized to generate a usable spectrum. Heating to 200° was generally sufficient. Each 70 eV spectra was obtained by repeatedly scanning the 10-1000 amu mass range over a 15 second period while the sample was heated. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

4-Ethynylaniline.

4-Ethynylaniline was obtained from Dr. Norm Bilow, Hughes Aircraft Co., Culver City, CA as a tan crystalline solid, m.p. 104.5-105°.

3-Ethynylaniline.

This material was obtained in high purity as a colorless liquid from Dr. Norm Bilow, Hughes Aircraft Co., CA.

4-Ethynylphthalic Anhydride.

4-Ethynylphthalic anhydride was obtained from Dr. Edward Sabourin, Gulf Research and Development Co., Pittsburgh, PA, as a yellow solid, m.p. 120-122°.

Phthalic Anhydride.

Eastman reagent ACS grade phthalic anhydride was sublimed under vacuum to provide white needles, m.p. 130-131°.

Aniline.

Aniline was redistilled under nitrogen just prior to use to provide a colorless liquid.

N,N-Dimethylacetamide.

Glass distilled *N,N*-dimethylacetamide was obtained from Burdick and Jackson Laboratories Inc., Muskegon, Michigan and used as received and also redistilled under vacuum over calcium hydride.

N-(3-Ethynylphenyl)phthalimide.

3-Ethynylaniline (1.17 g., 0.01 mole) was added to a solution of phthalic anhydride (1.48 g., 0.01 mole) in glass distilled DMAC (25 ml.) and the resultant solution was stirred under nitrogen for 0.5 hour at ambient temperature and at 150° for 1 hour. The cooled pale yellow solution was poured into cold water (200 ml.) to precipitate a white solid (2.31 g., 94% yield), m.p. 203-205°. Analysis by hplc showed a single peak. Recrystallization from toluene (20 ml.) provided near-white needles (1.57 g., 68% recovery), m.p. 204-205° [Lit. (12) m.p. 201-203°]. Characterization is given in Tables I, II, and III.

N-Phenyl-4-ethynylphthalimide.

4-Ethynylphthalic anhydride (0.241 g., 1.4 mmoles) was added to a solution of aniline (0.231 g., 1.4 mmoles) in DMAC (10 ml.) and the resultant yellow solution was stirred under nitrogen at ambient temperature for 0.5 hour and at 150° for 1 hour. The cooled amber solution was poured into cold water (200 ml.) to precipitate a tan solid (0.31 g., 90% yield), m.p. 204-206°. Analysis by hplc showed a single peak. Recrystallization from methanol provided a light tan crystalline solid, m.p. 206-207°. Characterization is given in Tables I, II, and III.

N-(4-Acetylphenyl)phthalimide.

4-Ethynylaniline (1.17 g., 0.01 mole) was added to a solution of phthalic anhydride (1.48 g., 0.01 mole) in glass distilled DMAC (25 ml.) and the resultant yellow solution stirred under nitrogen at ambient temperature for 0.5 hour and at 150° for 1 hour. The cooled amber solution was poured into cold water (200 ml.) to precipitate a yellow solid (2.0 g.). Analysis by hplc showed two peaks which were identified as the ethynylimide (23%) and the acetylimide (77%). Recrystallization from toluene (100 ml.) afforded a granular yellow solid which was again recrystallized from toluene to yield *N*-(4-acetylphenyl)phthalimide as a pale yellow solid, m.p. 239-240.5°. Characterization is given in Tables I, II and III. The yellow filtrate from precipitation of the yellow solid was cooled to provide bright yellow needles (0.3 g.)

identified as *N*-(4-acetylphenyl)-2-carboxybenzamide. Characterization is given in Tables I, II, and III.

N-(4-Ethynylphenyl)phthalimide.

4-Ethynylaniline (1.7 g., 0.01 mole) was added to a solution of phthalic anhydride in glass distilled DMAC (25 ml.) and the resultant yellow solution stirred under nitrogen at ambient temperature for 0.5 hour. The yellow solution was added dropwise during ~ 10 min. to a refluxing solution of acetic anhydride (30 ml.) and pyridine (2 ml.). After complete addition, the solution was heated under reflux for 0.5 hour, cooled, and poured into cold water (350 ml.). A granular crystalline tan solid precipitated (2.4 g., 97% yield) which showed a single peak upon analysis by hplc. Recrystallization from absolute ethanol (120 ml.) afforded light tan needles (1.5 g., 63% recovery) of *N*-(4-ethynylphenyl)phthalimide, m.p. 164-165°. Characterization is reported in Tables I, II, and III.

Attempted Hydration of 4-Ethynylaniline.

4-Ethynylaniline (0.1 g.) was heated separately in glass distilled DMAC (10 ml.), DMAC containing 0.5% water, and DMAC containing 5% water for 24 hours. The DMAC solution was poured into cold water and extracted with chloroform which was subsequently thoroughly washed with water and dried over calcium sulfate. The chloroform was evaporated to leave yellowish orange needles of 4-ethynylaniline. No 4-acetylaniline was detected.

Attempted Hydration of *N*-(4-ethynylphenyl)phthalimide.

N-(4-Ethynylphenyl)phthalimide (0.2 g.) was refluxed separately in DMAC (10 ml.) containing 0.1% water and 0.10 g. of benzoic acid, DMAC containing 0.5% water, and DMAC containing 5% water for 24 hours. The DMAC solution was poured into cold water to precipitate an off-white solid which was identified as starting material. No evidence for hydration of the ethynyl group was detected.

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(11) An equimolar mixture of *N*-(4-acetylphenyl)phthalimide and *N*-(4-ethynylphenyl)phthalimide was analyzed by hplc (Figure 1). The extinction coefficient of *N*-(4-ethynylphenyl)phthalimide at 254 nm was found to be greater than that of *N*-(4-acetylphenyl)phthalimide. The amounts of the acetyl and ethynyl imides reported were determined by normalizing peak heights to resolve the difference in extinction coefficients.

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