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(21) International Application Number: PCT/US92/00001 (22) International Filing Date: 2 January 1992 (02.01.92) (30) Priority data: 639,784 10 January 1991 (10.01.91) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventor: RENNER, Carl, Andrew ; 12 Brandywine Boulevard, Wilmington, DE 19809 (US). (74) Agents: FEENY, Charles, E. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH (European patent), CI (OAPI patent), CM (OAPI patent), CS, DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GA (OAPI patent), GB (European patent), GN (OAPI patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU (European patent), MC (European patent), MG, ML (OAPI patent), MN, MR (OAPI patent), MW, NL (European patent), NO, PL, RO, RU, SD, SE (European patent), SN (OAPI patent), TD (OAPI patent), TG (OAPI patent). Published <i>With international search report.</i>
(54) Title: BIS(AMINOPHENOXY)NAPHTHALENES AND BIS(NITROPHENOXY)NAPHTHALENES (57) Abstract Bis(aminophenoxy)naphthalenes, their preparation by catalytic reduction of bis(nitrophenoxy)naphthalenes with hydrogen and the preparation of bis(nitrophenoxy)naphthalenes from dihydroxynaphthalenes and chloronitrobenzene in a polar organic solvent such as dimethylacetamide using a basic catalyst such as potassium carbonate is disclosed. The preferred product compounds are 1,6-bis(4-aminophenoxy)naphthalene, 2,7-bis(4-aminophenoxy)naphthalene, 1,6-bis(4-nitrophenoxy)naphthalene and 2,7-bis(4-nitrophenoxy)naphthalene.		

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TITLE

BIS (AMINOPHENOXY) NAPHTHALENES
AND BIS (NITROPHENOXY) NAPHTHALENES

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FIELD OF THE INVENTION

The present invention relates to bis(aminophenoxy)naphthalenes which are derived from bis(nitrophenoxy)naphthalenes and the preparation of bis(nitrophenoxy)naphthalenes from dihydroxynaphthalenes with halonitrobenzenes. The bis(aminophenoxy)naphthalenes are made by the reduction of the corresponding bis(nitrophenoxy)naphthalenes.

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BACKGROUND OF THE INVENTION

Compounds of the type $\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{R}-\text{C}_6\text{H}_4-\text{NH}_2$

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where -R- is $-\text{O}-$, $-\text{C}(\text{CF}_3)_2-$, $-\text{C}(\text{CH}_3)_2-$, $-\text{CH}_2-$, $-\text{C}(=\text{O})-$,

are known in the art.

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Thermochim. Acta, 141, 77-88 Patel, R. H.,
Patel, V. S.; Patel, R. G. (1989) discloses 2,2-bis-
[4-(p-aminophenoxy)phenyl]-propane as a curing agent
for epoxy resins.

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JP 63/227616, 21 Sept. 1988, discloses
2,2-bis[4-(4-aminophenoxy)phenyl]propane.

JP 63/126848, 30 May 1988, discloses
4,4'-bis(3-nitrophenoxy)-3,3',5,5'-tetramethylbiphenyl
and reducing it.

U.S. 4,713,438 discloses alpha, alpha'-bis-
(p-aminophenyl)-4,4'-bis(isopropyl)biphenyl.

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JP 62/248635, 29 Oct. 1987, discloses
4,4'-bis(3-aminophenoxy)biphenyl and its use as a
monomer in preparing polyimides.

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PCT International Application No. WO 87/3871, 2 July 1987, discloses 4,4-bis(3-amino-phenoxy)biphenyl and 4,4'-bis(3-aminophenoxy)benzo-phenone.

5 European Patent Application 126494, 28 Nov. 1984, discloses 4,4'-bis(3-aminophenoxy)diphenyl sulfone.

U.S. 4,377,525 discloses 1,3-bis(3-amino-phenoxy)benzene for use as a monomer in preparing polyimides.

10 U.S. 4,064,107 discloses p,p'-bis(4-amino-phenoxy)diphenyl ether.

SUMMARY OF THE INVENTION

15 The present invention relates to 1,6-bis(4-aminophenoxy)naphthalene, 1,6-bis(4-nitro-phenoxy)naphthalene, 2,7-bis(4-nitrophenoxy)naphtha-lene, 2,7-bis(4-aminophenoxy)naphthalene, and their preparation. The preparation involves reacting 20 1,6-dihydroxynaphthalene or 2,7-dihydroxynaphthalene with para-nitrochlorobenzene in a polar organic solvent, such as dimethylacetamide, and a base, such as potassium carbonate. The product diamino compounds are useful as monomers in the preparation of 25 polyamides and polyimides.

DETAILED DESCRIPTION OF THE INVENTION

The bis(nitrophenoxy)naphthalenes of the present invention are made by reaction of 30 dihydroxynaphthalenes with a halonitrobenzene in a polar organic solvent in the presence of a base. Suitable polar organic solvents include N,N-dimethylacetamide, N,N-dimethylformamide,

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m-cresol, dimethyl sulfoxide and N-methylpyrrolidone. Of these, N,N-dimethylacetamide is the preferred solvent. Suitable bases include the hydroxides, carbonates, bicarbonates, hydrides and lower alkoxides, of the alkali metals, particularly potassium, sodium and lithium. Of these, potassium carbonate is the preferred base. Generally the reaction medium will contain from 2 to 19 weight percent and preferably 10 to 15 weight percent dihydroxynaphthalene. The mole ratio of dihydroxynaphthalene to halonitrobenzene present is about 0.9:2 to about 1.1:2 and preferably about 1:2. The amount of base present (calculated as K_2CO_3) is preferably from 86 to 250 weight percent and preferably 86 to 130 weight percent, as based on dihydroxynaphthalene present. Generally the temperature is from 110° to 165°C with from 135° to 155°C being the preferred range. The pressure is not critical and may be varied from 0.8 to 40 atmosphere. Atmospheric pressure is preferred for economic reasons.

If a solvent, such as N,N-dimethylacetamide, in which the bis(4-nitrophenoxy)naphthalene is not soluble, the product can be separated from the solvent and base by filtration. In other cases the solvent can be removed by distillation and the basic catalyst by extraction with a solvent which doesn't dissolve the product bis(4-nitrophenoxyphenyl)naphthalene.

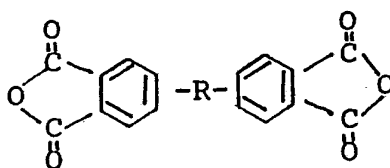
The bis(4-nitrophenoxyphenyl)naphthalene is reduced to bis(4-aminophenoxy)naphthalene using hydrogen and a solid hydrogenation catalyst. Suitable hydrogenation catalysts include palladium, platinum, nickel and rhodium. Preferably the hydrogenation catalyst is a solid so that it can be readily separated from the product

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bis(4-aminophenoxy)naphthalene by filtration. In a continuous mode the bis(4-nitrophenoxy)naphthalene can be melted and fed over a fixed bed of the hydrogenation catalyst along with hydrogen gas.

5 Generally the hydrogenation reaction is carried out at 50° to 150°C with 80° to 120°C being the preferred range. The hydrogen pressure in the reactor generally will be from 1 to 600 psig (6.9 to 4200 kPag) with 50 to 400 psig (345 to 2758 kPag) being the preferred
10 range. The hydrogenation reaction can be carried out in a solvent such as 1-butanol, 2-butanol, N,N-dimethyl acetamide, 2-methoxyethanol, tetrahydrofuran, N,N-dimethylformamide or N-methylpyrrolidone.

15 The product bis(4-aminophenoxy)naphthalene can be reacted with dicarboxylic acids or dianhydrides of tetracarboxylic acids to make polyamides or polyimides which are useful in preparing gas
20 separation membranes. The resulting gas separation membranes are useful in separating a variety of gases but the most interesting one from a commercial viewpoint is separating nitrogen and oxygen from mixtures thereof such as air to produce nitrogen and oxygen of sufficient purity to be useful industrially.
25 To produce nitrogen and oxygen of industrial grades, it generally is necessary to use the membranes serially arranged to provide a plurality of separation stages. The aromatic polyimides produced by reaction of 1,6-bis(4-aminophenoxy)naphthalene or
30 2,7-bis(4-aminophenoxy)naphthalene and bridged aromatic dianhydrides of the formula



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where -R- is $\begin{array}{c} \text{CF}_3 \\ | \\ -\text{C}- \\ | \\ \text{CF}_3 \end{array}$, $\begin{array}{c} \text{O} \\ || \\ -\text{C}- \end{array}$, -O-, -CH₂-, etc

5 and are soluble in a number of polar aprotic organic solvents such as N-methylpyrrolidinone, dichloromethane, dimethylsulfoxide and N,N-dimethylacetamide. This eliminates the need to form a shaped article product from a polyamic acid precursor which is then
10 converted by chemical and/or thermal means to effect ring closure and form the polyimide. The need to convert a shaped article formed of the polyamic acid precursor to the final polyimide severely limits the thickness of products that can be made.

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EXAMPLE 1

Preparation of 1,6-Bis(4-nitrophenoxy)naphthalene

To a 2-liter, four neck, round bottom flask equipped with a mechanical stirrer, thermometer with a
20 Thermowatch, a condenser and a nitrogen supply was added 1,6-dihydroxynaphthalene (250 g, 1.54 mole), potassium carbonate (250 g, 1.81 mole), p-nitrochlorobenzene (505 g, 3.20 mole) and 875 ml of dimethylacetamide. The reaction mixture was heated to 150°C and
25 the course of the reaction followed by thin layer chromatography. After 3 hours and 15 minutes the mixture was allowed to cool to 115°C, and then poured into two 2-liter erlenmeyer flasks, equipped with magnetic stirrers, each of which flasks contained 1200
30 ml of water at 70°C. After cooling to 45°C the product was isolated from both erlenmeyer flasks by filtering through a 3-liter fritted glass funnel. The product was washed five times with hot water and once with deionized water. After drying in a vacuum oven
35 at 80°C and 125 mm Hg absolute for eight hours, 607.8

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g (98% yield) of a yellow-tan crystalline solid was obtained which had a melting point of 188-190°C and a purity of 99.9% as determined by gas chromatography.

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EXAMPLE 2

Preparation of 1,6-Bis(4-aminophenoxy)naphthalene

To a 1-liter stirred titanium autoclave was added 1,6-bis(4-nitrophenoxy)naphthalene (200 g, 0.498 mole), 6 g of decolorizing carbon, 2 ml of concentrated ammonium hydroxide, 0.80 g of 5% palladium on carbon wet with water (dry weight 0.40 g) and 500 ml of 1-butanol. In a barricade, the vessel was heated to 115°C. Hydrogen gas was fed in beginning at 80°C. At 150 psig (1034 kPag) hydrogen uptake stopped. The pressure was raised to 400 psig (2758 kPag) and held for thirty minutes. The contents of the autoclave were poured under nitrogen to a 2-liter, three necked flask equipped with a mechanical stirrer, thermometer with a Thermowatch, which flask contained 600 ml of 1-butanol and 4 ml of 85% hydrazine hydrate in water at 80°C. The autoclave was rinsed out with 100 ml of additional 1-butanol which was added to the 2-liter flask. The mixture in the 2-liter flask was brought to a slow reflux. When all of the product was in solution, the contents of the 2-liter flask was vacuum transferred to a 2-liter round bottom flask through a fritted glass filter covered with Celite® filtering aid. After the transfer, the contents of the second flask were heated to 105°C giving a clear solution. The second flask was cooled to 0°C (crystallization of product began at 80°C). The product was isolated by filtering through a fritted glass filter funnel, washed twice with 600 ml of hot water and one with 600 ml of deionized water. After drying overnight in a vacuum oven at 100°C and 125 mm Hg absolute pressure,

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127.7 (76.2% yield) of a tan crystalline solid was obtained which had a melting point of 163°-164°C and no observable impurities by gas chromatography.

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EXAMPLE 3

Preparation of 2,7-Bis(4-nitrophenoxy)naphthalene

To a 2-liter, four necked round bottom flask equipped with a mechanical stirrer, Dean-Stark trap topped with a condenser, thermometer with a Thermowatch, heating mantle and nitrogen supply were added 2,7-naphthalenediol (200 g, 1.23 mole), potassium carbonate (200 g, 1.43 mole, 60 mesh), p-nitrochlorobenzene (400 g, 2.53 mole) and 700 ml of dimethylacetamide. Heating was begun and the temperature was raised to 150°C in 20 minutes, an exotherm was observed at 138°C. The temperature was held at 150°C and the reaction followed by thin layer chromatography. After four hours the reaction was complete. The mixture was cooled to 120°C and then poured into two 2-liter erlenmeyer flasks, each of which contained 1200 ml of water at 60°C. The mixtures precipitated and were stirred for 30 minutes then poured into a 3-liter fritted glass. The crude product was washed with 2 liters of hot water five times and once with 2 liters of methanol. After drying in a vacuum oven overnight at 80°C and 125 mm Hg absolute, 500.1 g (100.8% of theoretical) which had a melting point of 163-164°C. This product was sufficiently pure to make excellent demonstrations. Purification of a portion of this product by dissolving in hot xylenes, treating with decolorizing carbon and then crystallizing gave a pale yellow crystalline solid which had a melting point of 169-170.5°C.

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EXAMPLE 4

Preparation of 2,7-Bis(4-aminophenoxy)naphthalene

To a one liter titanium stirred autoclave were added 2,7-bis(4-nitrophenoxy)naphthalene (100 g, 0.249 mole), 5% palladium on carbon wet with water (0.40 g) (0.20 g dry weight), decolorizing carbon (2 g), concentrated ammonium hydroxide (1 ml) and 1-butanol (250 ml). The autoclave was heated to 110°C and hydrogen was fed in beginning at 80°C. Absorption appeared to cease at 140 psig (965 kPag). The pressure was raised to 400 psig (2758 kPag) and held for 30 minutes. The reaction mixture along with a wash of 200 ml 1-butanol was poured into a 2-liter, four necked flask equipped with a mechanical stirrer, heating mantle, thermometer with a Thermowatch, a condenser and a nitrogen supply, which flask contained 500 ml of 1-butanol and 2 ml of 85% hydrogen hydrate in water at 120°C. The mixture was heated to reflux. When the product in the flask was in solution, the mixture was vacuum transferred to a second similarly equipped flask through a steam jacketed enclosed fritted glass funnel which had a bed of Celite® filtering aid. After the transfer, the solution was heated to give a clear solution, then successively cooled by air, water and ice to 0°C. Crystallization began at 95°C. The product was isolated by filtering through a fritted glass filter, washed with 300 ml of hot water twice and with 300 ml of deionized water after drying in a vacuum oven overnight at 100°C and 125 mm Hg absolute, 70.2 g (82.5% yield) of a light yellow-tan solid was obtained which had a melting point of 172-173°C and was pure by gas chromatographic analysis.

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CLAIMS:

1. Bis(aminophenoxy)naphthalenes.
- 5 2. A compound of Claim 1 which is a
bis(4-aminophenoxy)naphthalene.
3. A compound of Claim 2 which is
1,6-bis(4-aminophenoxy)naphthalene.
- 10 4. A compound of Claim 2 which is
2,7-bis(4-aminophenoxy)naphthalene.
5. Bis(nitrophenoxy)naphthalenes.
- 15 6. A compound of Claim 5 which is a
bis(4-nitrophenoxy)naphthalene.
7. A compound of Claim 6 which is
20 1,6-bis(4-nitrophenoxy) naphthalene.
8. A compound of Claim 6 which is
2,7-bis(4-nitrophenoxy)naphthalene.

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INTERNATIONAL SEARCH REPORT

PCT/US 92/00001

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C07C217/90; C07C205/38		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C07C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP,A,0 387 203 (CIBA-GEIGY) 12 September 1990 see claims; example 11 ---	1,2,4
X	EP,A,0 357 558 (CIBA-GEIGY) 7 March 1990 see claims 1,15,16 ---	1-8
A	GB,A,2 229 180 (BRITISH PETROLEUM) 19 September 1990 see whole document ---	1-8
A	GB,A,2 148 279 (MITSUI TOATSU CHEMICALS INC.) 30 May 1985 see claims; examples ---	1-8
A	EP,A,0 192 480 (MITSUI TOATSU CHEMICALS INC.) 27 August 1986 see claims; examples ---	1-8
¹⁰ Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
23 APRIL 1992	06 MAY 1992	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	HELPS I.M. <i>I.M. Helms</i>	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9200001
SA 55903

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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