This invention relates to a novel aromatic diamine and more particularly to the use of said diamine for the preparation of thermally stable high-molecular weight polymers including, for example, polyamides, polyamideimides, polyimides, and the like. This diamine is obtained by reacting a stoichiometric amount of a disodium salt of 2,2-bis(4-hydroxyphenyl) hexafluoropropane with 4-chloronitrobenzene to obtain an intermediate, 2,2-bis[4-(4-nitrophenoxy)phenyl] hexafluoropropane, which is reduced to the corresponding 2,2-bis[4-(4-aminophenoxy)phenyl] hexafluoropropane.

1 Claim, No Drawings
DESCRIPTION OF THE PREFERRED EMBODIMENTS

PREPARATION OF A HIGH MOLECULAR WEIGHT DIAMINE HAVING THE FORMULA:

\[
\text{H}_2\text{N} - \text{O} \text{CF}_3 \text{C} \text{O} \text{O} \text{C} \text{N}_2
\]

is initiated by reacting stoichiometric amounts of 2,2-bis(4-hydroxyphenyl) hexafluoropropane with sodium hydroxide to produce the disodium salt according to the following:

\[
\text{CF}_3 \text{O} \text{H} \text{NaOH} \rightarrow \text{CF}_3 \text{O} \text{Na} \text{O} \text{C} \text{N}_2
\]

This reaction produces an intermediate compound which is sufficiently active to enter into a nucleophilic displacement reaction with the chloro-substituent on 4-chloronitrobenzene to produce 2,2-bis[4-(4-nitrophenoxyl)phenyl] hexafluoropropane according to the following:

\[
\text{O}_2\text{N} \text{Cl} \rightarrow \text{CF}_3 \text{O} \text{Na} \text{O} \text{C} \text{N}_2 \text{NO}_2 + 2\text{NaCl}
\]

Reduction of the dinitro compound to the corresponding diamine is accomplished by reacting the compound in the presence of activated iron and water, stannous chloride, or hydrogen with a palladium catalyst.

The following example teaches the preferred method of synthesizing 2,2-bis[4-(4-amino phenoxyl)phenyl] hexafluoropropane.

EXAMPLE I

Approximately 26.9 gm (0.08 mole) of 2,2-bis(4-hydroxyphenyl) hexafluoropropane was dissolved in 120 gm of dimethyl acetamide and 60 ml toluene containing 6.8 gm (0.17 mole) sodium hydroxide and 3 ml water. The mixture was heated to reflux and the water was removed by means of a Dean-Stark trap. After all of the water was removed, the toluene was removed by distillation until the pot temperature reached 150° C.

To the disodium salt prepared above in 150 g dimethyl acetamide was added 31.51 g (0.2 mole) 4-chloronitrobenzene. The reaction mixture was heated at 150° C. for 48-hours and then poured into 1000 ml wa-
The yellow precipitate was collected by filtration and washed well with water. Recrystallization from ethanol afforded 43 g (93%) of \(\text{2,2-bis}[4-(4\text{-nitrophenoxy})\text{-phenyl}]\) hexafluoropropane; mp 158°-160° C. A mixture of 11.56 g (0.02 mole) \(\text{2,2-bis}[4-(4\text{-nitrophenoxy})\text{-phenyl}]\) hexafluoropropane, 8.96 g (0.16 mole) powdered iron and 20 ml of ethanol were added to a 100 ml three-necked flask. The mixture was heated to reflux and then a solution of 0.14 ml (6 mmole) of hydrochloric acid in 5 ml of ethanol was added dropwise with vigorous stirring. The mixture was refluxed for two-hours, then made alkaline to litmus by adding alcoholic potassium hydroxide. The mixture was filtered hot and the filter cake was boiled twice with fresh ethanol to remove all of the amine. The filtrate was cooled and 300 ml of concentrated hydrochloric acid was added. The resulting amine hydrochloride was collected by filtration and washed with ethanol. The dihydrochloride then was dissolved in water (150 ml) and 5 percent (w/v) sodium hydroxide was added until the mixture was alkaline to litmus. The insoluble diamine was collected by filtration and then recrystallized from ethanol to give 6.3 g of nearly colorless needles; mp 150°-152° C.

**ANALYSIS:** Calculated for \(\text{C}_{27}\text{H}_{20}\text{N}_{2}\text{O}_{2}\text{F}_{6}\): C, 62.43; H, 3.94; N, 5.27. Found: C, 62.55; H, 3.88; N, 5.40.

As suggested previously, this diamine can be used to produce polyimides or polyamides when reacted with a diamic acid, a dianhydride, or a diacid halide. Because of the fluorine substituent on the diamine, the resulting polyimides or polyamides have improved chemical and thermal stability.

The following example illustrates the use of the diamine to prepare a polyimide resin product.

**EXAMPLE II**

To a stirred solution of 1.04 g (2 mmole) of \(\text{2,2-bis}[4-(4\text{-aminophenoxy})\text{-phenyl}]\) hexafluoropropane in 4.0 g of dimethylacetamide was slowly added portionwise 0.645 g (2 mmole) of benzophenone tetracarboxylic acid dianhydride (BTDA) at such a rate that each portion of dianhydride was allowed to dissolve before the next portion was added. The reaction was run under a nitrogen blanket and was cooled with a water bath. The residual BTDA was washed into the reaction flasks with an additional 3 ml of dimethylacetamide to give a 19 percent by weight solids solution. The reaction mixture was stirred for three hours after the last of the BTDA had been added and then was transferred to a vacuum oven. The solvent was removed at 100° C. and the resulting amide/acid polymer was imidized by heating it to 180° C. for four hours. The tough flexible polymer was found to have an inherent viscosity of 0.47 dl/g (H\(_2\)SO\(_4\) at 30° C.). Initial weight loss occurred at 420° C. in a TGA scan in air.

We claim:

1. An aromatic diamine compound having the structure;

\[
\text{H}_2\text{N}*=\begin{array}{ccc}
\text{O} & \text{O} & \text{O} \\ \\
\text{CF}_3 & \text{CF}_3 & \text{NH}_2
\end{array}
\]