Methyl- and Fluoro-Substituted Bis(4'-aminophenoxy)benzenes: A Convenient Method of Synthesis

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Abstract: We have synthesised a series of new bis(ether amine)s, primarily 1,2-bis(4'-aminophenoxy)benzene derivatives but including 1,3- and 1,4-bis(4'-aminophenoxy)benzene derivatives, with fluoro and alkyl substituents. These diamines were synthesised by fluoro displacement with 1-fluoro-4-nitrobenzene or its derivatives, or nitro displacement with 1,4-dinitrobenzene, and various phenylenediols and their alkyl- or fluoro-substituted derivatives. The resulting bis(ether nitro) compounds were reduced to the corresponding bis(ether amine)s. Thus, various bis(4'-aminophenoxy)benzenes were prepared which can be used in the synthesis of polyimides, polyamides and poly(azomethine)s with different distributions of alkyl and fluoro substituents and different substituent patterns, enabling a comprehensive study of structure-property relationships to be undertaken.

Key words: fluoro displacement, dihydroxybenzenes, 3,4-difluoronitrobenzene, synthesis, fluoronitrotoluene, bis(4-aminophenoxy)benzenes

Bis(4'-aminophenoxy)benzenes with the general formula:



are aminophenyl derivatives of simple aromatic diols, i.e. hydroquinone, resorcinol, catechol and certain dihydroxynaphthalenes. These diamines are of considerable interest to the polymer chemist, because their incorporation into relatively stiff aromatic polymer chains may provide flexibility and enhance processability. The synthesis of 1,4bis(4'-aminophenoxy)benzene was described by Arcoria and Passerini¹ while 1,3-bis(4'-aminophenoxy)benzene was subsequently prepared by Williams et al. using a solvent-assisted Ullmann synthesis.² These compounds, derivatives of hydroquinone and resorcinol and known as TPE-Q and TPE-R diamines, respectively, are now widely used in the polymer field. The use of both TPE- Q^3 and TPE-R⁴ diamines in polyimides was described several years ago. Much later, diamines derived from catechol, namely 1,2-bis(2'- and 4'-aminophenoxy)benzene and related substances with aminopyridyl units, were described by Kurita and Williams;⁵ synthesis was by chloro displacement in the presence of potassium tert-butoxide and reported yields were low, extensive purification was needed and the diamines were not widely used. The use of 1,2bis(2'- and 3'-aminophenoxy)benzene in the synthesis of polyimides has been reported.⁶ Now, with a better understanding of nucleophilic aromatic displacement reactions, we are able to demonstrate that the synthesis of pure 1,2bis(4'-aminophenoxy)benzenes and their derivatives, as well as corresponding 1,3- and 1,4-bis(4'-aminophenoxy)benzenes, has become a relatively easy task. Bis(4'-

nitrophenoxy)benzenes, precursors to the diamines, can be synthesised easily by halo displacement from 4-halonitrobenzenes, or by nitro displacement using 1,4-dinitrobenzene.

Our previous finding that modifying substitution patterns, especially by incorporating catechol and substituted moieties, modified the processability of both poly(ether imide)s and poly(ether amide)s from solution or melt, especially when combined with alkyl and fluoro substituents,^{7,8} led us to become interested in bis(4'aminophenoxy)benzenes bearing different numbers of methyl or fluoro substituents. We wished to synthesise diamines with the substituents distributed in different ways in the molecules and present in either the central or terminal rings of the diamine moiety or, alternatively, distributed more evenly throughout the molecule. No diamines of this type are reported in the Beilstein database.⁹ Recently. another specific diamine with *p*-phenoxyamine units linked ortho to an aromatic residue, 2,3-bis(4'-aminophenoxy)naphthalene, has been synthesised by Yang and Chen;¹⁰ the diamine was prepared by a chloro displacement reaction between 1-chloro-4-nitrobenzene and 2,3dihydroxynaphthalene followed by reduction of the resulting dinitro compound. This diamine and 1,2-bis(4'aminophenoxy)benzene have been used in the synthesis of polyamides.^{10, 11}

Here we report the synthesis of a number of methyl- and fluoro-substituted diamines based on simple aromatic diols and principally 1,2-dihydroxybenzenes; some new diamines were also prepared from derivatives of hydroquinone and resorcinol for use in comparative studies of polymer properties. Diamines in which the central ring had alkyl or fluoro substituents were synthesised from variously substituted diols and 1-fluoro-4-nitrobenzene, with subsequent reduction of the product. Diamines with methyl substituents in the outer rings were similarly synthesised from fluoronitrotoluenes and either unsubstituted or substituted diols. Fluoro substitution in the outer rings was achieved by employing 1,2-difluoro-4-nitrobenzene; the nomenclature scheme adopted is a selfconsistent scheme which allows us to identify reactants used and products formed unambiguously, see the Scheme. The fluorine in the 2'-position, i.e. meta to the nitro group, is practically unreactive under the conditions used, in dimethylformamide solution in the presence of potassium carbonate at 130°C, and remains intact. This contrasts with the synthesis of related dinitriles and diacids where we found that fluoro meta to nitrile is very reactive relative to the corresponding nitro compounds.¹² This







Scheme

study therefore generalises and completes the syntheses of substituted bis(4'-aminophenoxy)benzenes from hydroquinone, resorcinol and catechol derivatives from commercially available diols in order to provide monomers for studies of structure–property relationships in several types of polymers.

For all syntheses of dinitrophenoxy ethers reported here we preferred to use fluoro-displacement reactions from fluoronitrobenzenes rather than the less expensive chloronitrobenzenes, used in some previous cases, because of the higher yields and purity of the products.

The diamines described in this paper have now been used in the synthesis of poly(ether imide)s, poly(ether amide)s and poly(azomethine)s with a variety of dianhydrides, diacids and dialdehydes, respectively. The synthesis and properties of those polymers will be presented separately where the effects of different substitution patterns (i.e. *ortho-, meta-* and *para-*linkages), as well as the influences of alkyl and fluoro substituents, on polymer properties will be compared.

Results and Discussion

The overall reaction scheme employed for the synthesis of bis(ether amine)s is summarised in the Scheme where, in the first step, 1-fluoro-4-nitrobenzene (1a) or a derivative **1b–d** is reacted with a dihydroxybenzene or substituted derivative **2A,B,C,i–viii**, in the presence of potassium carbonate, to produce a bis(4'-nitrophenoxy)benzene derivatives **3**. Reactions were carried out with hydroquinone derivatives **2Ai**, **2Aii**, **2Aviii**, resorcinol derivatives **2Bi**, **2Bii**, and catechol derivatives **2Ci**, **2Ciii**, **2Civ**, **2Cv**, **2Cvi**, **2Cvii**. In all cases the reactions proceeded readily to give high yields, often greater than 90%, of bis(4'-nitrophenoxy)benzene compound; crystallisation solvents and

melting points and yields of the products are given in Tables 1, 3 and 5. In all cases results of C,H,N analyses were in excellent agreement with calculated values. In one case, the synthesis of **3aBii** from 2-methylresorcinol, the displacement was undertaken with 1,4-dinitrobenzene; this reaction was also highly efficient and gave a high yield of product after two hours reaction.

Fluoro displacements from **1a,c,d** are relatively straightforward, only one mode of displacement and formation of ether linkage is possible. With 1b two modes of displacement are potentially feasible. It is normally considered that the nitro group will activate a para fluorine and not a meta fluorine for nucleophilic displacement. However, we recently demonstrated that a nitrile group will activate meta fluorine towards displacement in the presence of potassium carbonate in aprotic solvents, albeit at a higher temperature than was necessary for efficient para-fluorodisplacement reactions.¹² In supplementary experiments we have demonstrated that fluoro displacement from 1fluoro-4-nitrobenzene is efficient but displacement from 1-fluoro-3-nitrobenzene does not occur under comparable conditions. Thus, the fluoro displacement from 1,2-difluoro-4-nitrobenzene should be selective with only the para-fluoro group being displaced. This proved to be the case in displacement reactions involving **1b** where with 2Ai, 2Bi, 2Ci, and 2Cv only one fluorine was displaced, see NMR data later.

All of the bis(4'-nitrophenoxy)benzenes prepared were readily reduced by hydrazine in the presence of palladium on charcoal catalyst; yields of the corresponding diamines were mostly in excess of 90% and always greater than 80%. Melting points, crystallisation solvents and yields are presented in Tables 2, 4 and 5; C, H, N analyses, in all cases, gave results in excellent agreement with calculated values. Identification of compounds by elemental analysis data were confirmed by accurate mass determinations; the results for three compounds are given in Table 6.

That, in the case of fluoro displacement from 1,2-difluoro-4-nitrobenzene, only the para fluorine was displaced while the meta fluorine remained intact was confirmed by analysis of NMR spectra. Tables 6 and 7 present the results of an analysis of NMR spectra for bis(4'-aminophenoxy)benzenes produced from the products of fluoro displacement from 1,2-difluoro-4-nitrobenzene and hydroquinone, resorcinol and catechol, i.e. 4bAi, 4bBi, and **4bCi**, respectivelly. The assignments are based on 1 H (400 and 300 MHz), ¹⁹F (235 and 280 MHz) and ¹³C (100 and 75 MHz) spectra with COSY 2-D proton-proton correlations for 4bBi and 4bCi and HECTOR C-H correlations for 4bAi and 4bBi. In all cases the chemical shifts, splitting patterns and coupling constants are consistent with structures 5 and inconsistent with the isomeric structures 6. For example, F-H couplings are consistent with coupling of F with one ortho, one meta and one para H, as expected for 5, whereas 6 would require one ortho and two meta couplings. Other features are also inconsistent with **6**, e.g. the calculated chemical shift for C(2') in **5** is $\delta =$ 154.8, with a strong C-F coupling, consistent with the observed doublet at 155.8 and a coupling constant of 242 Hz, while the calculated chemical shift for C(2') in (6) is $\delta = 144.4$; there is no peak near this position with strong coupling to F.



Thus, we have established an efficient route to a wide variety of new diamines which can be used as monomers in the synthesis of several varieties of aromatic polymers, namely polyimides, polyamides and poly(azomethine)s. The various aromatic substitution patterns on the central aromatic ring and the dispositions of different numbers and locations of alkyl and fluoro substituents gives rise to a considerable family of materials which are being used in the assessment of structure–property relationships.

All chemicals were used as supplied by major companies including Aldrich, Fluka and Fluorochem.

The procedures used for the synthesis of the dinitro compounds **3** and subsequent conversion to diamines **4** were identical for all combinations of fluoronitrobenzenes and diols used. The details of a single reaction sequence are described below. The only differences between

the syntheses detailed, that is the syntheses of 1,2-bis(4'-nitrophenoxy)benzene and of 1,2-bis(4,-aminophenoxy)benzene, and the procedures used for other combinations were in the recrystallisation solvents used, which are given in the tables detailing the mps and yields of the products.

Mps were determined with a Mettler FP-5/FP-50 hot stage attached to a polarizing microscope using a heating rate of 1 °C min⁻¹ and values quoted are uncorrected. ¹H and ¹³C NMR spectra were recorded (in Liverpool) on a Bruker AMX-400 spectrophotometer, while ¹⁹F spectra were recorded on a Bruker WM250 spectrometer operating at 235 MHz. Accurate molar masses were determined on a VG Analytical 7070E spectrometer. Masses of molecular ions were also determined on a TRIO-100 spectrometer.

Synthesis of 1,4-, 1,3- and 1,2-Bis(4'-nitrophenoxy)benzenes and Their Derivatives by F1uoro Displacement; General Procedure: In a three-necked round-bottomed flask, equipped with thermometer, Dean–Stark trap, magnetic stirring bar and nitrogen inlet, were placed DMF (100 mL) and the required diol (0.05 mol). The solution was thoroughly deoxygenated with a stream of N₂. Anhyd K₂CO₃ (12 g) was added, followed by sufficient toluene or xylene (usually 10– 15 mL) to enable the solution to boil at 130–135 °C. Under a stream of N₂, the mixture was brought to the boil and was dewatered (1– 1.5 h). After cooling to 60–70 °C, 1-fluoro-4-nitrobenzene (0.1 mol, plus 10% excess)(or fluoronitrotoluene, in relevant examples) was added and the mixture was again brought to the boil. The mixture was

Table 1. Characteristics and Analytical Data for 1,2-Bis(4'-nitrophenoxy)benzene and Derivatives^a

| Substance | | mp (°C) | Yield | |
|-----------|---|--|-------|--|
| Structure | Designation | (Solvent) | (%) | |
| 3aCi | 1,2-bis(4'-nitrophen- oxy)benzene | 134–135 (EtOH) | 98 | |
| 3aCv | 3-fluoro-1,2-bis(4'-nitro- phenoxy)benzene | 128.8–130.0 (EtOH) | 85 | |
| 3aCiii | 3-methyl-1,2-bis(4'-nitro- phenoxy)benzene | 117.5–119.0 (EtOH) | 73 | |
| 3aCiv | 4-methyl-1,2-bis(4'-nitro- phenoxy)benzene | 112–113 (EtOH) | 94 | |
| 3aCvi | 4- <i>tert</i> -butyl-1,2-bis(4'- nitrophenoxy)benzene | 147.2–147.9 (EtOH) | 92 | |
| 3aCvii | 3,5-di- <i>tert</i> -butyl-1,2- bis(4'-nitrophenoxy)ben- zene | 170.8–171.4 [EtOH/toluene (90:10)] | 96 | |
| 3cCi | 1,2-bis(2'-methyl-4'-nitro- phenoxy)benzene | 152.4–152.8 (EtOH) | 91 | |
| 3dCi | 1,2-bis(3'-methyl-4'-nitro- phenoxy)benzene | 105.6–107.7 (EtOH) | 83 | |
| 3dCiv | 4-methyl-1,2-bis(3'-meth- yl-4'-nitrophenoxy)ben- zene | 82-84 (EtOH) | 61 | |
| 3bCi | 1,2-bis(2'-fluoro-4'-nitro- phenoxy)benzene | 149–151 (EtOH) | 90 | |

 a Satisfactory elemental analysis obtained: C \pm 0.29, H \pm 0.04, N \pm 0.08.

| phenony)o | | | | |
|-----------|--|---|--------------------|--|
| Substance | | mp (°C) | Yield | |
| Structure | Designation | (Solvent) | (%) | |
| 4aCi | 1,2-bis(4'-aminophen- oxy)benzene | 135–136 (EtOH) 137–138 ^b | 94 (85 pure) | |
| 4aCv | 1,2-bis(4'-aminophen- oxy)-3-fluorobenzene | 99–101 (MeOH) | 86 | |
| 4aCiii | 1,2-bis(4'-aminophen- oxy)-3-methylbenzene | 114.3–115.5 (MeOH) | 93 | |
| 4aCiv | 1,2-bis(4'-aminophen- oxy)-4-methylbenzene | 164.4–165.0 (EtOH) | 85 | |
| 4aCvi | 1,2-bis(4'-aminophen- oxy)-4- <i>tert</i> -butylbenzene | 131–132 (EtOH) | 88 | |
| 4aCvii | 1,2-bis(4'-aminophen- oxy)-3,5-di- <i>tert</i> -butyl- benzene | 166–167 [(1) EtOH, (2) cy- clohexane] | 82 | |
| 4cCi | Ci 1,2-bis(4'-amino-2'- methylphenoxy)benzene | 126.5–127.0 (cyclohexane/ toluene) | 93 | |
| | | | | |

Table 2. Characteristics and Analytical Data for 1,2-Bis(4'-aminophenoxy)benzene and Derivatives⁴

| | | 137–138 ^b | pure) |
|--------|--|---|-------|
| 4aCv | 1,2-bis(4'-aminophen- oxy)-3-fluorobenzene | 99–101 (MeOH) | 86 |
| 4aCiii | 1,2-bis(4'-aminophen- oxy)-3-methylbenzene | 114.3–115.5 (MeOH) | 93 |
| 4aCiv | 1,2-bis(4'-aminophen- oxy)-4-methylbenzene | 164.4–165.0 (EtOH) | 85 |
| 4aCvi | 1,2-bis(4'-aminophen- oxy)-4- <i>tert</i> -butylbenzene | 131–132 (EtOH) | 88 |
| 4aCvii | 1,2-bis(4'-aminophen- oxy)-3,5-di- <i>tert</i> -butyl- benzene | 166–167 [(1) EtOH, (2) cy- clohexane] | 82 |
| 4cCi | Ci 1,2-bis(4'-amino-2'- methylphenoxy)benzene | 126.5–127.0 (cyclohexane/ toluene) | 93 |
| 4dCi | 1,2-bis(4'-amino-3'- methylphenoxy)benzene | 123–124 (EtOH) | 94 |
| 4dCiv | 1,2-bis(4'-amino-3'- methylphenoxy)-4- methylbenzene | 128–130 (MeOH) | 94 |
| 4bCi | 1,2-bis(4'-amino-2'-fluo- rophenoxy)benzene | 51–152 (MeOH) | 93 |

^a Satisfactory elemental analysis obtained: C \pm 0.18, H \pm 0.15, N \pm 0.26.

^b Lit. ref 5.

| Table 3. | Characteristics | and Analytical | Data for 1,4 | -Bis(4'-nitrophen- |
|----------|--------------------|----------------|--------------|--------------------|
| oxy)ben | zenes ^a | | | |

| Substance | | mp (°C) | Yield |
|-----------|--|-----------------------|-------|
| Structure | Designation | (Solvent) | (%) |
| 3aAii | 2-methyl-1,4-bis(4'-nitro- phenoxy)benzene | 201–202 (BuOH) | 92 |
| 3aAviii | 2,3,5-trimethyl-1,4- bis(4'-nitrophenoxy)ben- zene | 193–194 (BuOH) | 92 |
| 3bAi | 1,4-bis(2'-fluoro-4'-nitro- phenoxy)benzene | 192–193 (BuOH) | 92 |
| 3cAviii | 2,3,5-trimethyl-1,4- bis(2'-methyl-4'-nitro- phenoxy)benzene | 24–225 (BuOH/EtOH) | 96 |

 a Satisfactory microanalysis obtained: C \pm 0.17, H \pm 0.07, N \pm 0.05.

refluxed for 3-4 h. Subsequently, some toluene (or xylene) was distilled off and the mixture was poured into a stirred ice-water mixture (1.5 L). Stirring was continued for a few hours or overnight; the products sometimes solidified very slowly. The product, as a solid crystalline mass, was filtered off and washed a few times with water. The wet cake was dissolved in boiling EtOH, with added Norit decolourising agent, and was crystallised. This crystallisation procedure applies to all 1,2- and 1,3-diols used. In the case of the nitrophenoxy derivatives of 1,4-diols the crude product was washed with MeOH (on a filter) and was recrystallised (boiling BuOH) after decolourisation. Most dinitro compounds so synthesised were pale yellow, highly crystalline substances; the resorcinol derivatives were colourless. Yields and melting points are presented in Tables 1, 3 and 5. The same procedure was used in the reaction of 2-methylresorcinol with 1,4-dinitrobenzene.

Synthesis of 1,4-, 1,3- and 1,2-Bis(4,-aminophenoxy)benzenes and Their Derivatives; General Procedure:

1,2-Bis(4'-nitrophenoxy)benzene (0.03 mol), synthesised as described above, was dissolved, or partially dissolved/suspended, in EtOH (800-1200 mL). For 1,4- and 1,3-bis(4'-nitrophenoxy)benzenes, or derivatives, less EtOH was satisfactory. To the boiling solu-

Table 4. Characteristics and Analytical Data for 1,4-Bis(4'-aminophenoxy)benzenes^a

| Substance | | mp (°C) (EtOH) | Yield |
|-----------|---|-------------------|-------|
| Structure | Designation | (Lton) | (70) |
| 4aAii | 1,4-bis(4'-aminophen- oxy)-2-methylbenzene | 102–103 | 92 |
| 4aAviii | 1,4-bis(4'-aminophen- oxy)-2,3,5-trimethylben- zene | 190–191 | 99 |
| 4bAi | 1,4-bis(4'-amino-2'-fluo- rophenoxy)benzene | 226.5-227 | 95 |
| 4cAviii | 1,4-bis(4'-amino-2'- methylphenoxy)-2,3,5- trimethylbenzene | 230.4–231 | 93 |

^a Satisfactory microanalysis obtained: $C \pm 0.19$, $H \pm 0.01$, $N \pm 0.04$.

Table 5. Characteristics and Analytical Data for 1,3-Bis(4'-nitrophenoxy)benzenes and 1,3-Bis(4'-aminophenoxy)benzenes^a

| Substance | | $mp(^{\circ}C)$ | Yield | |
|-----------|--|---|-----------------|--|
| Structure | Designation | (Sorvent) | (%) | |
| 3aBii | 2-methyl-1,3-bis(4'-nitro- phenoxy)benzene | 155.0–155.7 (EtOH) | 83 ^b | |
| 4aBii | 1,3-bis(4'-aminophen- oxy)-2-methylbenzene | 52.2–152.6 (MeOH) | 80 | |
| 3bBi | 1,3-bis(2'-fluoro-4'-nitro- phenoxy)benzene | 81–82 (MeOH) | 85 | |
| 4bBi | 1,3-bis(4'-amino-2'fluo- ro-phenoxy)benzene | 113.4–114.1 [toluene/cyclo- hexane (1:3)] | 82 | |

^a Satisfactory microanalysis obtained: $C \pm 0.13$, $H \pm 0.03$, $N \pm 0.06$. ^b Synthesised by nitro displacement from 1,4-dinitrobenzene in DMF in the presence of K₂CO₃ at 130 °C, 2 h.

| | Accurate Mass (Dalton) Observed | | | Calculated |
|---------------------|---------------------------------|--------------------------|--------------------------------------|------------|
| | 4bAi 328.1017 | 4bBia 328.1017 | 4bCi ^a 328.1020 | 328.1023 |
| δ | | | | |
| H (2, 3, 5, 6) | 6.89 | | | 6.72 |
| H (2) | | 6.56 | | 6.37 |
| H (4, 6) | | 6.52 | | 6.42 |
| H (5) | | 7.13 | | 7.07 |
| H (3, 6) | | | ~6.82 | 6.72 |
| H (4, 5) | | | ~6.92 | 6.77 |
| H (3') | 6.63 | 6.49 | 6.50 | 6.12 |
| H (5') | 6.53 | 6.40 | 6.40 | 6.20 |
| H (6') | 6.94 | 6.91 | 6.92 | 6.56 |
| F (2') | -127.9 | | | |
| J (Hz) | | | | |
| $J_{2-4.6}$ | | ~2.3 | | |
| $J_{5-4.6}^{2-4,0}$ | | ~8.1 | | |
| $J_{3'5'}$ | 2.53 | 2.69 | 2.69 | |
| $J_{5'6'}$ | 8.69 | 8.55 | 8.79 | |
| J _{3' F} | 13.34 | 11.96 | 11.96 | |
| $J_{5'F}$ | 1.23 | 1.23 | 1.22 | |
| J _{6' F} | 9.38 | 8.78 | 8.79 | |

Table 6. Accurate Molar Masses, ¹H and ¹⁹F NMR Chemical Shifts (δ) and Coupling Constants

^a See ref 13.

Table 7. ¹³C NMR Chemical Shifts (δ) and Coupling Constants

| | Observed | | | Calculated |
|---------------------|----------|-------------------|-------------------|------------|
| | 4bAi | 4bBi ^a | 4bCi ^a | |
| δ | | | | |
| C (1, 4) | 154.7 | | | 152.6 |
| C (2, 3, 5, 6) | 117.4 | | | 120.7 |
| C (1, 3) | | 159.9 | | 157.7 |
| C (2) | | 104.4 | | 109.7 |
| C (4, 6) | | 109.4 | | 114.0 |
| C (5) | | 129.9 | | 131.7 |
| C (1, 2) | | | 148.0 | 148.3 |
| C (3, 6) | | | 117.2 | 120.7 |
| C (4, 5) | | | 123.0 | 125.0 |
| C (1') | 133.1 | 134.1 | 135.3 | 135.0 |
| C (2') | 155.8 | 155.2 | 154.7 | 154.8 |
| C (3') | 102.6 | 103.7 | 103.8 | 103.9 |
| C (4') | 148.4 | 144.6 | 144.0 | 143.6 |
| C (5') | 110.8 | 110.8 | 110.7 | 112.3 |
| C (6') | 124.2 | 123.9 | 123.0 | 121.4 |
| J (Hz) | | | | |
| $J_{1'-\mathrm{F}}$ | 12.8 | 11.7 | 11.3 | |
| $J_{2'-\mathrm{F}}$ | 242 | 240.6 | 240.2 | |
| $J_{3'-F}$ | 20.8 | 21.2 | 21.7 | |
| $J_{4'-\mathrm{F}}$ | 9.4 | 9.6 | 9.1 | |
| $J_{5'-\mathrm{F}}$ | 1.6 | | 2.9 | |
| J _{6'-F} | 3.2 | | | |

^a See ref 13.

tion/suspension, 10% Pd/C (0.3 g) was added. To the mixture, boiling under reflux, hydrazine monohydrate (35 mL) was added over a period of 1 h. Refluxing was continued for a period of 3 h after which the catalyst was filtered off from the colourless hot solution of diamine. The volume of the solution was reduced to 10% by rotary evaporation. The diamine was precipitated by addition of water and was filtered off and washed twice with water. The wet diamine cake was recrystallised from the smallest possible volume of EtOH to yield, usually, snow-white diamine of monomer purity. Some diamines based on methyl-substituted catechols are very soluble and were recrystallised (MeOH) and the mother liquor was worked up to recover the full yield of product. Yields and mps are presented in Tables 2, 4 and 5.

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