Synthesis of multinuclear asymmetrical diamines based on 4-(nitrophenoxy)phthalic acids

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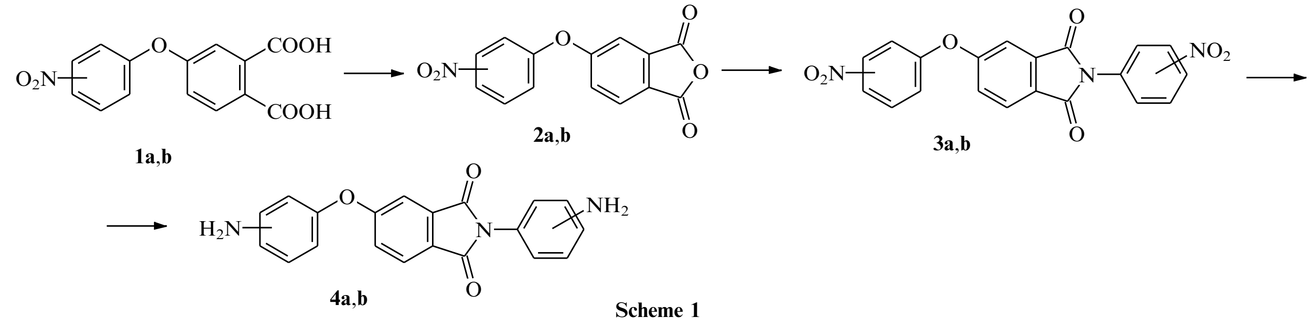
Four new *N*-(aminophenyl)-4-(aminophenoxy)phthalimides, which can be used as monomers for the preparation of polyimides, have been synthesised from 4-(*p*- and *m*-nitrophenoxy)phthalic acids.

The syntheses of 4-(*p*- and *m*-aminophenoxy)phthalic acids (APPA) as well as the syntheses and properties of polyimides based on them have been reported.[1–6] The last stage in the preparation of APPA is the catalytic reduction of the corresponding nitrophthalic acids with hydrogen.

In the present study the intermediates 4-(*p*-nitrophenoxy)phthalic acid **1a** and 4-(*m*-nitrophenoxy)phthalic acid **1b** were used to prepare a series of *N*-(aminophenyl)-4-(aminophenoxy)phthalimides **4a**–**d** (Scheme 1).[†]

4-(*p*- and *m*-Nitrophenoxy)phthalic anhydrides **2a**,**b** were prepared by dehydrating **1a**,**b**.[‡] Treatment of **2a**,**b** with *p*- and *m*-nitroanilines affords **3a**–**d** with the terminal nitro groups in different positions.[§] The last stage in the preparation of **4a**–**d** involves the liquid-phase catalytic reduction of **3a**–**d** with

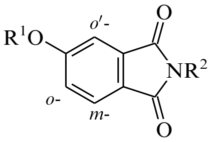


Scheme 1

Table 1 Melting points and yields for **4a**–**d**.

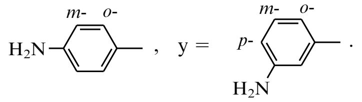
Compound	Mp/°C	Solvent for recrystallisation	Yield (%)
N-(*p*-aminophenyl)-4-(*p*-aminophenoxy)phthalimide **4a**	240–242	dioxane–hexane (4 : 1)	89
N-(*m*-aminophenyl)-4-(*m*-aminophenoxy)phthalimide **4b**	185–186	benzene–hexane (5 : 1)	88
N-(*p*-aminophenyl)-4-(*m*-aminophenoxy)phthalimide **4c**	188–190	benzene–hexane (5 : 1)	92
N-(*m*-aminophenyl)-4-(*p*-aminophenoxy)phthalimide **4d**	205–207	dioxane–hexane (3 : 1)	84

Table 2 Interpretation of the ^1H NMR spectra of compounds **4a**–**d**.[a]



R^1	R^2	^1H NMR δ/ppm ([$^2H_6$]DMSO)
x	x	7.96 *m*-1H, 7.29dd *o*-1H, 7.14d *o′*-1H, 6.97d *o*-2H(R^2), 6.88 *o*-2H(R^1), 6.65d *m*-2H(R^2), 6.61d *m*-2H(R^1), 5.32 NH_2(R^2), 5.17 NH_2(R^1).
x	y	7.88d *m*-1H, 7.31dd *o*-1H, 7.16d *o′*-1H, 7.11t *m*-1H(R^2), 6.88d *o*-2H(R^1), 6.66d *m*-2H(R^1), 6.61d *o*-1H(R^2), 6.53 *o′*-1H(R^2), 6.53d *o*-1H(R^2), 6.48d *p*-1H(R^2), 5.27 NH_2(R^2), 5.19 NH_2(R^1).
y	x	7.89d *m*-1H, 7.37dd *o*-1H, 7.26d *o′*-1H, 7.11t *m*-1H(R^1), 6.98d *o*-2H(R^2), 6.62d *m*-2H(R^2), 6.47d *p*-1H(R^1), 6.37d *o′*-1H(R^1), 6.26d *o*-1H(R^1), 5.37 NH_2(R^1), 5.33 NH_2(R^2).
y	y	7.92d *m*- 1H, 7.38dd *o*-1H, 7.28d *o′*-1H, 7.11t *m*-1H(R^1), 7.11t *m*-1H(R^2), 6.60d *o*-1H(R^2), 6.54d *o*-1H(R^2), 6.49d *p*-1H(R^1), 6.49d *p*-1H(R^2), 6.32d *o′*-1H(R^1), 6.27d *o*-1H(R^2), 5.37 NH_2(R^1), 5.29 NH_2(R^2).

[a] For R^1 and R^2: x =



hydrogen.[¶] The IR spectra of **4a**–**d** exhibit the following absorption bands (Vaseline oil, cm^{-1}): 3380–3350 and 3250–3200 (ν_{NH}), 1780–1770 and 1705–1700 ($\nu_{C=O}$), and 1250–240 ($\nu_{C–O}$). The R_f values found for the TLC of compounds **4a**–**d** with the same eluent as has been used for **3a**–**d** are 0.20–0.25.[††] More detailed data for compounds **4a**–**d** are presented in Tables 1 and 2. Polyimides are usually synthesised from symmetrical diamines.[12–14] A distinctive feature of compounds **4a**–**d** is that they do not possess any intrinsic symmetry.

[†] Compounds **1a**,**b** were prepared by condensation of 3,4-xylenol with *p*-nitrochlorobenzene or with *m*-dinitrobenzene in an aprotic dipolar amide solvent in the presence of K_2CO_3 followed by oxidation of 4-(*m*- and *p*-nitrophenoxy)-*o*-xylenes with nitric acid under an elevated pressure or with oxygen in acetic acid in the presence of a mixed cobalt-bromide catalyst by known procedures.[4–7] Mp for **1a** 167–169 °C (from 15% acetic acid); for **1b** 159–160 °C (from water).

[‡] *General procedure for the synthesis of* **2a**,**b**. Compounds **1a**,**b** were heated under reflux in a 10-molar excess of acetic anhydride for 2 h after which the acetic anhydride was completely evaporated under reduced pressure. 4-(*p*-Nitrophenoxy)phthalic anhydride **2a**, mp 129–131 °C (from acetic anhydride), yield 92%; 4-(*m*-nitrophenoxy)phthalic anhydride **2b**, mp 116–118 °C (from acetone), yield 93%. The compounds **2a**,**b** have satisfactory elemental analyses and expected IR spectra.

[§] *General procedure for the synthesis of* **3a**–**d**. Compound **2a** or **2b** was boiled for 2 h with *p*- or *m*-nitroaniline in acetic acid (1 : 1, 0.4 mol dm^{-3}). The reaction mixture was cooled, the precipitate was filtered off, washed with acetic acid until the filtrate was colourless, and dried. *N*-(*p*-Nitrophenyl)-4-(*p*-nitrophenoxyphthalimide) **3a**, mp 273–274 °C, Yield 90%; *N*-(*m*-nitrophenyl)-4-(*m*-nitrophenoxy)phthalimide **3b**, mp 192–194 °C, yield 84%; *N*-(*p*-nitrophenyl)-4-(*m*-nitrophenoxy)phthalimide **3c**, mp 195–197 °C, yield 84%; *N*-(*m*-nitrophenyl)-4-(*p*-nitrophenoxy)phthalimide **3d**, mp 232–233 °C, yield 88%. Compounds **3a**–**d** have satisfactory elemental analyses. IR for **3a** (Vaseline oil, cm^{-1}): 1520, 1345 (ν_{NO_2}), 1780, 1705 ($\nu_{C=O}$), 1254 ($\nu_{C–O}$). TLC of compounds **3a**–**d** (petroleum ether : acetone : benzene : acetic acid = 10 : 10 : 5 : 1 as eluent): $R_f = 0.70$.

[¶] *General procedure for the synthesis of* **4a**–**d**. Liquid-phase catalytic reduction of **3a**–**d** was carried out with hydrogen in DMF or dioxane with stirring at 100 °C and a hydrogen pressure of 2.0 MPa. The initial concentration of **3a**–**d** was 0.5 mol dm^{-3} and 40 g 5% Pd/C per mole of **3a**–**d** was used as the catalyst. The process was carried out for 0.5–1.0 h until hydrogen was no longer absorbed. The 5% Pd/C catalyst was prepared according to a known procedure.[8] Previously we noted that the addition of water to an organic solvent for the liquid-phase catalytic reduction of a wide range of organic nitro-derivatives leads to an increase in the reaction rate and in the yield and purity of the resulting amino-derivatives.[9–11] Therefore, the syntheses of **4a**,**c**,**d** were carried out in DMF to which 2.0 mol dm^{-3} of water was added. When the reaction was complete, the catalyst was filtered off, the solution was mixed with a threefold excess of water, and the precipitate filtered off and dried. This procedure is not entirely suitable for **4b**, because when the reaction solution is mixed with water, the target diamine precipitates as an oil. Hence, **4b** is preferably obtained in dioxane. In this case, after separation of the catalyst, dioxane is evaporated under reduced pressure without heating, and **4b** is isolated as a solid precipitate and recrystallised from solvent mixtures listed in Table 1.

Among other reasons, this is due to the nonequivalent positions of the amino groups in the terminal phenyl fragments.

Previously it has been shown in relation to APPA that the loss of the intrinsic symmetry leads to an increase in the solubility of polyimides, *i.e.* facilitates their processing, their thermal and mechanical properties being maintained at the same level.[1–3] It may be expected that the combination of amino groups, benzene rings, an oxygen bridge and an imide ring occurring in **4a**–**d** would lead to new and interesting properties of polyimides based on them.

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