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

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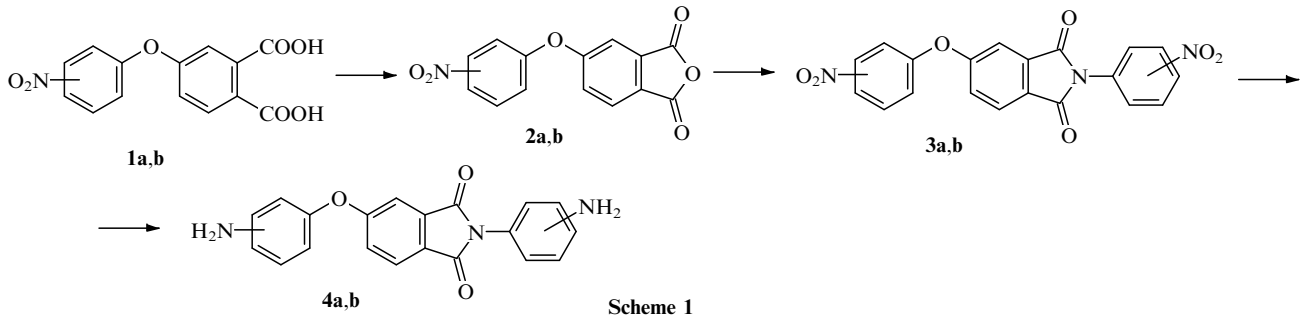
Four new *N*-(aminophenyl)-4-(aminophenoxy)phthalimides, which can be used as monomers for the preparation of polyimides, have been synthesised from 4-(*p*- and *m*-nitrophenoxy)phthalic acids.

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 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 (ν_{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.[7–14] A distinctive feature of compounds **4a–d** is that they do not possess any intrinsic symmetry. Among other reasons, this is due to the nonequivalent positions of the amino groups in the terminal phenyl fragments.

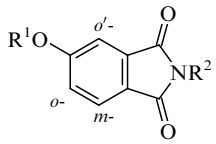


Scheme 1

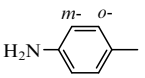
Table 1 Melting points and yields for **4a–d**.

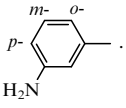
Compound	Mp/°C	Solvent for recrystallisation	Yield (%)
N-(*p*-aminophenyl)-4-(*p*-aminophenoxy)phthalimide **4a**	240–242	dioxane–hexane (4 : 1)	89
N-(*m*-aminophenyl)-4-(*m*-aminophenoxy)phthalimide **4b**	185–186	benzene–hexane (5 : 1)	88
N-(*p*-aminophenyl)-4-(*m*-aminophenoxy)phthalimide **4c**	188–190	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 ^{1}H NMR spectra of compounds **4a–d**.[a]



R^1	R^2	^{1}H 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 = 

, y = 

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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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† 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 (ν_{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.