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Investigation of 2,6-disubstituted *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamines as precursors/building blocks for molecular magnets

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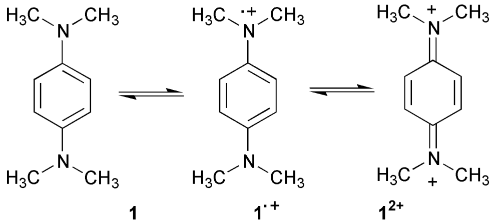
The synthesis of 2,6-disubstituted *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamines (R = Cl, Br, I, CN, or $C\equiv CSi(CH_3)_3$), potential precursors/building blocks for molecular magnets, is presented. In addition to standard methods (^{1}H NMR, ^{13}C NMR, MS, IR, UV), the products were also characterised by means of cyclic voltammetry. Completely reversible electrochemical behaviour was observed for both the CN and the $C\equiv CSi(CH_3)_3$ derivatives. Moreover, the corresponding radical cations and the dications were observed by cyclic voltammetry for these compounds. The first oxidation step of the Cl and the Br derivatives was also found to be reversible, although a chemical side reaction was detected after oxidation to the corresponding dication. The radical cation could not be detected for the I derivative. In this case direct oxidation to the dication followed by a chemical reaction was observed.

Introduction

Interest in molecular materials with special physical properties has increased during recent decades. One area that is still growing focuses on magnetically active systems, so-called molecular magnets.[1–4] A major part of the reported work deals with metal–organic materials exhibiting such features as ferromagnetism and spin-crossover. Purely organic materials with unusual magnetic properties have also attracted increasing attention, for example neutral radicals or materials containing charged radicals.[2] Several experiments based on nitrogen radical cations have been reported as well as approaches employing compounds containing *p*-phenylenediamine units.[5–7] It is well known that this unit, *e.g.* *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine **1** (TMPD), can be oxidised to intensely deeply coloured cations (Wurster salts).[8–13] The first oxidation step leads to the formation of the stable blue radical cation $\mathbf{1}^{\bullet+}$ [eqn. (1)] which can be isolated, *e.g.* as $\mathbf{1}^{\bullet+}\cdot ClO_4^-$ (Wursters Blue). Further oxidation yields the diamagnetic dication $\mathbf{1}^{2+}$. The salt $\mathbf{1}^{\bullet+}\cdot ClO_4^-$ exhibits interesting behaviour. The material is paramagnetic at room temperature and “switches’ gradually to diamagnetism in the thermal range 100–200 K due to dimerisation.[14] A comparable behaviour—at higher temperature and with thermal hysteresis—has recently been reported for 1,3,5-trithia-2,4,6-triazapentalenyl.[15]



1 $\mathbf{1}^{\bullet+}$ $\mathbf{1}^{2+}$

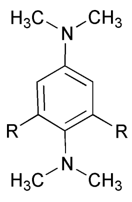
To date a rather high number of *p*-phenylenediamine derivatives and their corresponding radical cations have been described. In most cases the substituents at the nitrogen atoms and/or the counter ions have been varied.[5–7] Radical anions of *p*-phenylenediamine derivatives are also known, *e.g.* from *N*,*N*,*N*′,*N*′-tetrakis(trimethylsilyl)-*p*-phenylenediamine.[16] Fewer investigations have been carried out with compounds substituted at the aromatic ring.[12,17,18] In particular, *p*-phenylenediamines functionalised with halogens have rarely been described.[19]

In this work we present a series of 2,6-disubstituted TMPDs **2**. The synthesis of derivatives substituted with R = Cl, Br, I, CN, or $C\equiv CSi(CH_3)_3$, respectively, is discussed. The aim of this study was the synthesis of 2,6-disubstituted TMPDs **2** that can be used as precursors/building blocks for molecular magnets. Consequently, characterisation by means of cyclic voltammetry (CV) was performed to probe the stability of the corresponding radical cations.

Experimental

Characterisation

Melting points (uncorrected) were determined in open capillaries using a Büchi 530. ^{1}H NMR spectra were recorded on a

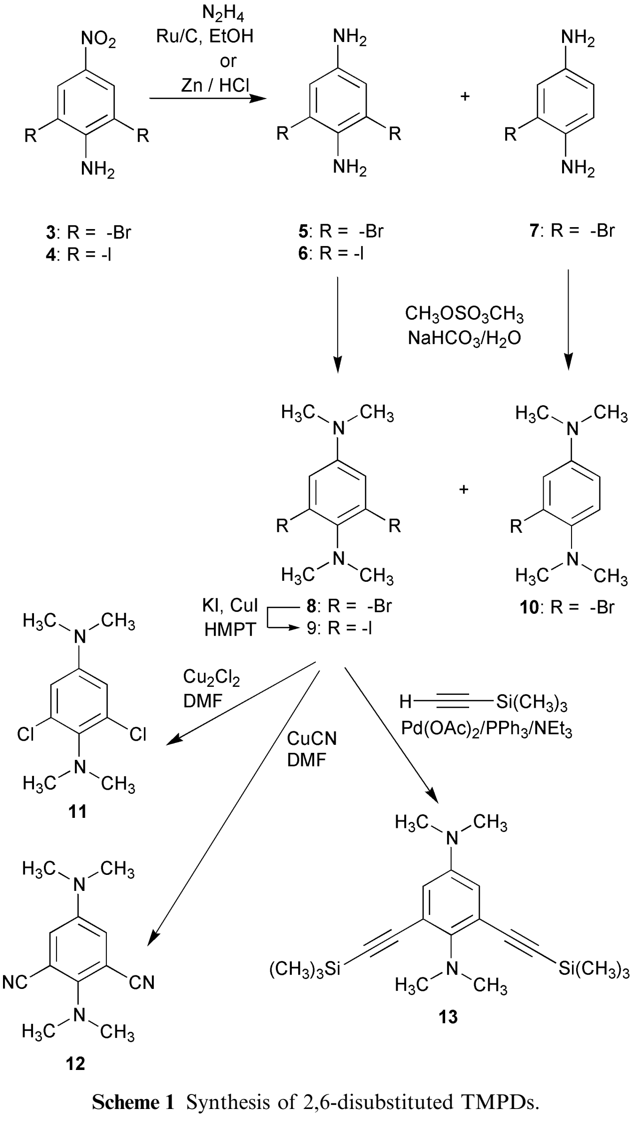


2

Bruker BH-S 90 FT-NMR spectrometer at 90 MHz or on a Bruker MSL 300 FT-NMR spectrometer at 300 MHz in $CDCl_3$ or acetone-d_6 (indicated in the data section). ^{13}C NMR spectra were measured on a Bruker MSL 300 FT-NMR spectrometer at 74.5 MHz in the same solvents. IR spectra were taken as KBr pellets on a Bomem Michelson 100 FTIR spectrometer. UV spectra were performed on a HP 8452A spectrometer using solutions in acetonitrile. EI mass spectra (70 eV) were recorded on a Kratos Profile double focusing magnetic sector field mass spectrometer equipped with direct insertion and GC (GC: Shimadzu GC-14A, column: HP-5MS). The isotope peak with highest natural abundance is reported. Cyclic voltammetry was performed on an EG&G PARC 263 potentiostat in acetonitrile with Pt as working electrode and an Ag/Ag^+ reference electrode. Bu_4NPF_6 (0.1 mol L^{-1}) was used as supporting electrolyte. The concentration of the analyte was 1.5 mmol L^{-1}. All results are reported *vs.* ferrocene which was measured prior to the samples.

Synthetic route

The synthetic route to the 2,6-disubstituted TMPD derivatives investigated in this work is shown in Scheme 1. 2,6-Dibromo-*p*-nitroaniline (**3**) and 2,6-diiodo-*p*-nitroaniline (**4**) were converted to 2,6-dibromo-*p*-phenylenediamine (**5**) and 2,6-diiodo-*p*-phenylenediamine (**6**), respectively. Changing reaction conditions allowed the preparation of 2-bromo-*p*-phenylenediamine (**7**) from aniline **3**. Methylation of the diamines **5–7** gave 2,6-dibromo-TMPD (**8**), 2,6-diiodo-TMPD (**9**) and 2-bromo-TMPD (**10**), respectively. Subsequent reactions with derivative **9** provided 2,6-dichloro-TMPD (**11**), 2,6-dicyano-TMPD (**12**) and 2,6-bis(trimethylsilylethynyl)-TMPD (**13**).



Scheme 1 Synthesis of 2,6-disubstituted TMPDs.

Materials

2,6-Dibromo-*p*-nitroaniline **3**, 2,6-diido-*p*-nitroaniline **4**, N_2H_4 (80% aq. solution), Ru (5% on carbon), palladium(II) acetate, PPh_3, and ethynyltrimethylsilane were used as obtained (highest quality available from Aldrich). All other inorganic compounds were obtained from Aldrich, Fluka or Merck (analytical grade). Solvents (Merck or Aldrich, analytical grade) were purified by conventional methods.[20] The silica gel used for column chromatography (>230 mesh ASTM) was obtained from Merck.

Synthesis

Reduction of 2,6-dibromo-*p*-nitroaniline 3 with Ru–N_2H_4. 2,6-Dibromo-*p*-phenylenediamine 5. 5.2 g (17.6 mmol) of aniline **3** were dispersed in 40 mL of ethanol. The reaction mixture was heated to 60 °C. 5 mL of N_2H_4 (80% aq. solution) and 0.3 g of ruthenium (5% on carbon, 0.15 mmol Ru) were added. The suspension was refluxed for 2 h. After evaporation of the solvent 20 mL of THF were added. The solution was filtered through silica gel. Evaporation of the solvent yielded 4.44 g (16.7 mmol, yield 95%) of 2,6-dibromo-*p*-phenylenediamine **5** as a yellow crystalline material; mp 137–138 °C (from THF); ^1H NMR (90 MHz, acetone-d_6) δ in ppm: 6.7 (s, arom. H); ^{13}C NMR (acetone-d_6) δ in ppm: 139.5 (arom. C_1), 134.7 (arom. C_4), 119.4 (arom. C_3, C_5), 110.1 (arom. C_2, C_6); MS, *m*/*z* in Da (rel. int.): 266 (100, M^+), 185 (33, $[M - Br]^+$), 106 (28, $[M - 2Br]^+$), 80 (32, $[HBr]^+$), 79 (28, Br^+); IR (KBr) ν/cm^{-1}: 3423, 3401, 3316, 3206, 1628, 1580, 1556, 1478, 1426, 1303, 1239, 1082, 1048, 918, 854, 840, 807; UV, λ_{max} in nm (ε in L mol^{-1} cm^{-1}): 206 (2.6×10^4), 214 (2.4×10^4), 249 (1.1×10^4), 334 (3.9×10^3); Anal. calcd. for $C_6H_6Br_2N_2$ (265.94): C 27.1, H 2.3, N 10.5; found: C 27.2, H 2.2, N 10.5%.

Analogous reduction of 2,6-diiodo-*p*-nitroaniline 4 with Ru–N_2H_4. 2,6-Diiodo-*p*-phenylenediamine 6. 5.0 g (12.8 mmol) of aniline **4** were converted to product **6** as described for the synthesis of **5**. 4.48 g (12.4 mmol, yield 97%, yellow crystals) of diamine **6** were obtained; mp 165–166 °C (from THF); ^1H NMR (90 MHz, acetone-d_6) δ in ppm: 7.1 (s, arom. H); ^{13}C NMR (acetone-d_6) δ in ppm: 139.6 (arom. C_1), 136.8 (arom. C_4), 126.8 (arom. C_3, C_5), 94.3 (arom. C_2, C_6); MS, *m*/*z* in Da (rel. int.): 360 (100, M^+), 233 (18, $[M - I]^+$), 106 (17, $[M - 2I]^+$); IR (KBr) ν/cm^{-1}: 3404, 3392, 3323, 3309, 3189, 1611, 1586, 1538, 1463, 1414, 1293, 1235, 1040, 861, 854, 846, 795; UV, λ_{max} in nm (ε in L mol^{-1} cm^{-1}): 194 (1.8×10^4), 212 (2.7×10^4), 228 (2.5×10^4), 253 (1.1×10^4), 336 (4.7×10^3); Anal. calcd. for $C_6H_6I_2N_2$ (359.94): C 20.0, H 1.7, N 7.8; found: C 20.0, H 1.8, N 7.9%.

Reduction of 2,6-dibromo-*p*-nitroaniline 3 with Zn–NH_4Cl. 2-Bromo-*p*-phenylenediamine 7. 30.0 g (101.4 mmol) of aniline **3** were dissolved in 420 mL of ethanol. 150 mL of water, 30 g (560 mmol) of NH_4Cl and 11.35 g (173 mmol) of Zn were added. The suspension was refluxed for 8 h. During this period an additional 12 g (183 mmol) of Zn were added in small portions. After additional 4 h refluxing, the suspension was filtered. The filtrate was acidified with hydrochloric acid to pH = 1–2. The solvent was removed *in vacuo*, the residue dispersed in 600 mL of 10% aq. K_2CO_3. The mixture was extracted three times with 400 mL of methylene chloride. The organic layers were combined and dried over Na_2SO_4. After evaporation of the solvent the crude product was purified by column chromatography (silica gel; eluent: methylene chloride). 12.68 g (67.8 mmol, yield 67%) of yellow crystalline diamine **7** were obtained; mp 75 °C (from methylene chloride); ^{1}H NMR (90 MHz, acetone-d_6) δ in ppm: 6.5–6.8 (m, arom. H); ^{13}C NMR (acetone-d_6) δ in ppm: 139.5 (arom. C_1), 136.6 (arom. C_4), 119.5 (arom. C_3), 117.3 (arom. C_6), 116.5 (arom. C_5), 110.6 (arom. C_2); MS, *m/z* in Da (rel. int.): 186 (100, M^+), 107 (27, $[M - Br]^+$), 80 (35, $[HBr]^+$), 79 (31, Br^+); IR (KBr) ν/cm^{-1}: 3408, 3292, 3189, 1615, 1577, 1500, 1433, 1315, 1302, 1237, 1152, 1077, 1028, 850, 819; UV, λ_{max} in nm (ε in L mol^{-1} cm^{-1}): 208 (1.8×10^4), 249 (1.1×10^4), 328 (3.3×10^3); Anal. calcd. for $C_6H_7BrN_2$ (187.04): C 38.5, H 3.8, N 15.0; found: C 38.7, H 3.8, N 15.1%.

Methylation of 2,6-dibromo-*p*-phenylenediamine 5. 2,6-Dibromo-*N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine 8

1.2 g (4.51 mmol) of diamine **5** were dispersed in 2.4 mL of water. 7.81 g (93 mmol) of $NaHCO_3$ were added. The mixture was cooled with ice and 2.92 mL (30.7 mmol) of dimethyl sulfate were added dropwise. After 50 minutes the ice bath was removed and the mixture was allowed to warm up to room temperature. Subsequently the reaction mixture was slowly heated to 65 °C and stirring was continued until the generation of CO_2 stopped. Subsequently, the suspension was diluted with 2.4 mL of cold water and 3 mL of ethanol amine. The temperature was increased to 140 °C, stirring was continued for 50 minutes. After cooling to room temperature 300 mL of H_2O were added. The aq. solution was extracted with methylene chloride (three times 150 mL). The organic fractions were combined and dried over Na_2SO_4. The residue obtained by evaporation was purified by column chromatography (silica gel; eluent: cyclohexane–ethyl acetate = 15 : 1). The yield of yellow crystalline 2,6-dibromo-TMPD **8** was 650 mg (2.02 mmol, yield 45%); mp 75–76 °C (from cyclohexane–ethyl acetate); ^{1}H NMR (90 MHz, acetone-d_6) δ in ppm: 2.8 (s, 6H, NMe_2), 2.9 (s, 6H, NMe_2), 6.7 (s, 2H, arom. H); ^{13}C NMR (acetone-d_6) δ in ppm: 150.52 (arom. C_1), 137.40 (arom. C_4), 127.46 (arom. C_3, C_5), 116.60 (arom. C_2, C_6), 42.24 (NMe_2), 40.29 (NMe_2); MS, *m/z* in Da (rel. int.): 322 (100, M^+), 307 (33, $[M - Me]^+$), 226 (18, $[M - MeBr]^+$), 160 (20, $[M - 2HBr]^+$); IR (KBr) ν/cm^{-1}: 2877 (Me), 1592 (arom. C=C), 1501, 1438, 1183, 1062 (Ph–Br), 971, 945, 824 (Ph–H), 735; UV, λ_{max} in nm (ε in L mol^{-1} cm^{-1}): 199 (2.7×10^4), 221 (2.4×10^4), 262 (1.4×10^4), 324 (2.7×10^3); Anal. calcd. for $C_{10}H_{14}Br_2N_2$ (322.04): C 37.3, H 4.4, N 8.7; found: C 37.2, H 4.4, N 8.8%.

Analogous methylation of 2,6-diiodo-*p*-phenylenediamine 6. 2,6-Diiodo-*N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine 9. 4.66 g (12.9 mmol) of diamine **6** were methylated as described above for the synthesis of product **8**. The yield of compound **9** was 1.3 g (3.13 mmol, yield 26%, pale yellow crystals); mp 63–64 °C (from cyclohexane–ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ in ppm: 2.8 (s, 6H, NMe_2), 2.9 (s, 6H, NMe_2), 7.2 (s, 2H, arom. H); ^{13}C NMR ($CDCl_3$) δ in ppm: 150.2 (arom. C_1), 143.01 (arom. C_4), 123.37 (arom. C_3, C_5), 101.94 (arom. C_2, C_6), 41.95 (NMe_2), 40.70 (NMe_2); MS, *m/z* in Da (rel. int.): 416 (100, M^+), 401 (7, $[M - Me]^+$), 274 (31, $[M - MeI]^+$); IR (KBr) ν/cm^{-1}: 2848 (Me), 1576 (arom. C=C), 1489, 1425, 1176, 1054 (Ph–Br), 950, 836 (Ph–H), 702; UV, λ_{max} in nm (ε in L mol^{-1} cm^{-1}): 221 (4.1×10^4), 234 (3.9×10^4), 265 (2.2×10^4), 320 (4.8×10^3); Anal. calcd. for $C_{10}H_{14}I_2N_2$ (416.05): C 28.9, H 3.4, N 6.7; found: C 28.9, H 3.3, N 6.7%.

Analogous methylation of 2-bromo-*p*-phenylenediamine 7. 2-Bromo-*N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine 10. Methylation of 12 g (64.2 mmol) of compound **7** gave 10.08 g (41.5 mmol, yield 65%) of yellow crystalline product **10**; mp 62–63 °C (from cyclohexane–ethyl acetate); ^{1}H NMR (90 MHz, acetone-d_6) δ in ppm: 2.6 (s, 6H, NMe_2), 2.8 (s, 6H, NMe_2), 6.5–6.9 (m, 3H, arom. H); ^{13}C NMR (acetone-d_6) δ in ppm: 149.1 (arom. C_1), 142.45 (arom. C_4), 122.24 (arom. C_3), 121.60 (arom. C_6), 117.97 (arom. C_5), 113.48 (arom. C_2), 44.89 (NMe_2), 40.75 (NMe_2); MS, *m/z* in Da (rel. int.): 242 (100, M^+), 227 (63, $[M - Me]^+$), 148 (24, $[M - MeBr]^+$); IR (KBr) ν/cm^{-1}: 2858 (Me), 1606 (arom. C=C), 1505, 1445, 1311, 1175, 1051 (Ph–Br), 1026, 956, 954, 834 (Ph–H), 808 (Ph–H); UV, λ_{max} in nm (ε in L mol^{-1} cm^{-1}): 212 (2.1×10^4), 265 (1.4×10^4), 324 (2.5×10^3); Anal. calcd. for $C_{10}H_{15}BrN_2$ (243.15): C 49.4, H 6.2, N 11.5; found: C 49.5, H 6.3, N 11.6%.

Reactions of 2,6-dibromo-TMPD 8 and 2,6-diiodo-TMPD 9. Conversion of compound 8 to derivative 9. 1.57 g (4.9 mmol) of 2,6-dibromo-TMPD **8** were dissolved in 60 mL of hexamethylphosphoric triamide. 12.08 g (63.3 mmol) of CuI and 14.41 g (92.9 mmol) of KI were added. The dispersion was refluxed for 25 h. Afterwards the brown suspension was cooled to room temperature and poured into 300 mL of H_2O. The precipitating crude products were filtered and washed twice with 20 mL of water. After drying *in vacuo* the product was purified by column chromatography (silica gel; eluent: cyclohexane). 850 mg (2.04 mmol, yield 42%) of pale yellow crystals of compound **9** were obtained (for analytical data compare methylation of **6**).

Reaction of compound 9 with Cu_2Cl_2. 2,6-Dichloro-*N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine 11. 1.0 g (2.4 mmol) of derivative **9** were dissolved in 20 mL of DMF and 1.2 g (12.1 mmol) of Cu_2Cl_2 were added. The reaction mixture was refluxed under Ar for 30 hours. The yellow solution turned red and precipitation occurred. After cooling to room temperature, 20 mL of NH_3 (28% aq. solution) were added. The mixture was again heated to reflux for 2 hours. The solution was cooled to room temperature, diluted with 200 mL of H_2O, and extracted three times with 100 mL of methylene chloride. The combined organic layers were dried over Na_2SO_4. The residue obtained after evaporation of the solvent was purified by column chromatography (silica gel; eluent: toluene) to give 201 mg (0.86 mmol, yield 36%) of pale yellow crystals of 2,6-dichloro-TMPD **11**; mp 53.5–54.5 °C (from toluene); ^{1}H NMR (90 MHz, acetone-d_6) δ in ppm: 2.8 (s, 6H, NMe_2), 3.0 (s, 6H, NMe_2), 6.6 (s, 2H, arom. H); ^{13}C NMR (acetone-d_6) δ in ppm: 149.73 (arom. C_4), 137.14 (arom. C_1), 135.23 (arom. C_3, C_5), 112.93 (arom. C_2, C_6), 42.51 (NMe_2), 40.24 (NMe_2); MS, *m/z* in Da (rel. int.): 232 (100, M^+), 217 (75, $[M - Me]^+$); IR (KBr) ν/cm^{-1}: 2890 (Me), 1602 (arom. C=C), 1500, 1435, 1177, 1058 (Ph–Cl), 982, 950, 796 (Ph–H); UV, λ_{max} in nm (ε in L mol^{-1} cm^{-1}): 216 (1.4×10^4), 265 (9.6×10^3), 324 (1.5×10^3); Anal. calcd. for $C_{10}H_{14}Cl_2N_2$ (233.14): C 51.5, H 6.1, N 12.0; found: C 51.5, H 6.2, N 11.9%.

Conversion of 2,6-diiodo-TMPD 9 with CuCN. 2,6-Dicyano-*N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine 12. 403 mg (0.97 mmol) of compound **9** were dissolved in 20 mL of DMF, 417 mg (4.65 mmol) of CuCN were added. The solution was refluxed under Ar for 20 hours. During cooling to room temperature precipitation occurred. The solvent was removed *in vacuo*. The residue was dissolved in 20 mL of methylene chloride. After filtration and drying over Na_2SO_4 the solvent was removed *in vacuo*. Purification of the crude product by column chromatography (silica gel, eluent: methylene chloride) gave 207 mg (0.97 mmol, yield 100%) of pale green crystals of **12**; mp 142–143 °C (from methylene chloride); ^{1}H NMR (90 MHz, acetone-d_6) δ in ppm: 2.9 (s, 3H, NMe_2), 3.1 (s, 3H, NMe_2), 7.2 (s, 2H, arom. H); ^{13}C NMR (acetone-d_6) δ in ppm: 147.72 and 147.45 (arom. C_1, C_4), 121.56 (arom. C_3, C_5), 117.87 (CN), 112.36 (arom. C_2, C_6), 44.01 (NMe_2), 40.29 (NMe_2); MS, *m/z* in Da (rel. int.): 214 (100, M^+), 199 (42, $[M - Me]^+$); IR (KBr)

ν/cm^{-1}: 3084, 2885 (Me), 2229 (C≡N), 1598 (arom. C=C), 1499, 1445, 1377, 1234, 1184, 938, 863 (arom. H); UV, λ_{max} in nm (ε in L mol^{-1} cm^{-1}): 206 (1.9×10^4), 229 (1.4×10^4), 303 (6.4×10^3), 390 (1.6×10^3); Anal. calcd. for $C_{12}H_{14}N_4$ (214.27): C 67.3, H 6.6, N 26.1; found: C 67.3, H 6.6, N 26.0%.

Palladium catalysed reaction of 2,6-diiodo-TMPD 9 with ethynyltrimethylsilane. *N*,*N*,*N*′,*N*′-Tetramethyl-2,6-bis(trimethylsilylethynyl)-*p*-phenylenediamine 13. 3.10 g (7.45 mmol) of derivative **9**, 280 mg (1.25 mmol) of palladium(II) acetate and 474 mg (1.8 mmol) of triphenylphosphine were dissolved in 150 mL of triethylamine and heated to 80 °C. After addition of 7 mL (4.87 g, 49.6 mmol) of ethynyltrimethylsilane the solution was heated to reflux. Subsequently 5 mg of CuI were added. The formation of a white precipitate started immediately. Refluxing was continued for 15 h. After cooling to room temperature the white precipitate was filtered off and washed twice with 50 mL of triethylamine. The combined filtrates were evaporated, the residue dissolved in 70 mL of methylene chloride. The solution was washed twice with 40 mL of aq. $KHSO_4$ (0.5 mol L^{-1}) and three times with 50 mL of H_2O. The combined organic layers were dried over Na_2SO_4 and evaporated. Purification of the residue by column chromatography (silica gel, eluent toluene–methylene chloride = 1 : 1) gave 2.14 g (6.01 mmol, yield 81%) of yellow crystals of compound **13**; mp 85–86 °C (from toluene–methylene chloride); ^{1}H NMR (300 MHz, $CDCl_3$) δ in ppm: 0.3 (s, 18H, $SiMe_3$), 2.9 (s, 6H, NMe_2), 3.0 (s, 6H, NMe_2), 6.8 (s, 2H, arom. H); ^{13}C NMR ($CDCl_3$) δ in ppm: 148.12 and 146.47 (arom. C_1, C_4), 121.08 (arom. C_3, C_5), 119.45 (arom. C_2, C_6), 105.11 (Ph-C≡), 97.89 (≡C-Si), 43.86 (NMe_2), 41.17 (NMe_2), 0.22 ($SiMe_3$); MS, *m*/*z* in Da (rel. int.): 356 (100, M^+), 341 (8, $[M - Me]^+$), 283 (58, $[M - SiMe_3]^+$), 73 (7, $[SiMe_3]^+$); IR (KBr) ν/cm^{-1}: 2958, 2862 (Me), 2150 (C≡C), 1590 (arom. C=C), 1490, 1248, 1002, 845 (Si–C); UV, λ_{max} in nm (ε in L mol^{-1} cm^{-1}): 241 (5.1×10^4), 253 (4.5×10^4), 293 (8.1×10^3), 380 (4.4×10^3); Anal. calcd. for $C_{20}H_{32}N_2Si_2$ (356.66): C 67.4, H 9.0, N 7.9; found: C 67.3, H 9.1, N 7.8%.

Results and discussion

Synthesis of 2,6-disubstituted TMPDs

The first reaction step was the reduction of 2,6-dibromo-*p*-nitroaniline **3** to 2,6-dibromo-*p*-phenylenediamine **5**. A possible method described in the literature employs $SnCl_2$–HCl as a reducing agent.[21] Since the reported yield was only 45%, two other approaches were examined: (i) reduction with hydrazine (catalyst: ruthenium, 5% on carbon) and (ii) reaction with Zn–NH_4Cl. The best results were obtained with N_2H_4–Ru, a method which has already been used for the reduction of other halogenated nitrobenzenes.[22] In this case, compound **3** was nearly quantitatively converted into diamine **5** (yield: 95%). Significant side reactions could not be observed, neither by mass spectrometry nor by thin layer chromatography. In contrast, the reduction of compound **3** with Zn–NH_4Cl in EtOH–H_2O gave diamine **5** with a yield of only 7% due to the rapid elimination of one bromine as soon as most of the starting material was consumed. However, in this manner 2-bromo-*p*-phenylenediamine **7** could be obtained with a yield of 67%. Consequently, the reaction with N_2H_4–Ru was also used to convert 2,6-diiodo-*p*-nitroaniline **4** to 2,6-diiodo-*p*-phenylenediamine **6** (yield: 97%).

The *p*-phenylenediamines **5**–**7** were methylated with dimethyl sulfate–$NaHCO_3$ in H_2O.[23] The yields of corresponding tetramethylated products correlated to the steric demands of the substituents in position 2 and 6, respectively. 2-Bromo-TMPD **10** could be obtained with a yield of 65%. Methylation of the sterically more hindered diamine **5** gave 2,6-dibromo-TMPD **8** in a 45% yield and 2,6-diiodo-TMPD **9** was obtained with a yield of 26%.

2,6-Dibromo-TMPD **8** and 2,6-diiodo-TMPD **9** were used as starting materials for subsequent substitution reactions. Preliminary investigations showed that compound **9** generally exhibits a significant higher reactivity. Exchange of the iodine atoms against chlorine or cyanide by reaction of **9** with CuX (X = Cl or CN) in DMF[24] gave the corresponding derivatives **11** and **12**, respectively. 2,6-Dicyano-TMPD **12** was obtained with a yield of 100%, while the yield of 2,6-dichloro-TMPD **3** was 36%. A similar reaction of 2,6-dibromo-TMPD **8** with CuI could also be used to prepare the diiodo-derivative **9** (yield: 42%).[25]

Depending on the stability of the corresponding radical cations $\mathbf{2}^{\bullet+}$ (see below), some of the derivatives of **2** discussed above could also be useful as low molecular weight building blocks for magnetically active systems (*e.g.* as the corresponding ClO_4^- salts or as electron donors in charge-transfer complexes). In addition, 2,6-diiodo-TMPD **9** could be a versatile precursor for the preparation of other molecular magnets due to the high reactivity of the iodine atoms. For example, Heck type reactions with bifunctional co-monomers are an approach to new conjugated polyradicals. The theoretical suitability of compound **9** for this type of reaction was tested by the palladium catalysed reaction with ethynyltrimethylsilane. Both iodine atoms of compound **9** could be exchanged against trimethylsilylethynyl groups using palladium(II) acetate–triphenylphosphine as a catalyst.[26,27] The yield of *N*,*N*,*N*′,*N*′-tetramethyl-2,6-bis(trimethylsilylethynyl)-*p*-phenylenediamine **13** was 81%. Base catalysed removal of the -$Si(CH_3)_3$ protection groups to give 2,6-diethynyl-TMPD, subsequent oxidative polymerisation and the Heck reaction of 2,6-diethynyl-TMPD with **9**, followed by oxidation of the *p*-phenylenediamine units; is currently under investigation with the aim of preparing conjugated polyradicals. However, the successful preparation of compound **13** indicates, that 2,6-diiodo-TMPD **9** is indeed a versatile precursor to conjugated polyradicals and other new molecular magnets.

Electrochemistry

The dichloro-compound **11** showed two well separated redox events. The important part of the corresponding cyclic voltammograms is reproduced in Fig. 1. The two regions of electrochemical activity are the first and second monoelectronic processes of the *p*-phenylenediamine unit.[10] This well known behaviour of this unit is shown for TMPD in eqn. (1). It has to be kept in mind that the rotation of one of the dimethylamino groups of **11** is hindered due to the 2,6 disubstitution. Consequently, the dications of the 2,6-disubstituted TMPDs can obviously not have the planar structure of the dication $\mathbf{1}^{2+}$

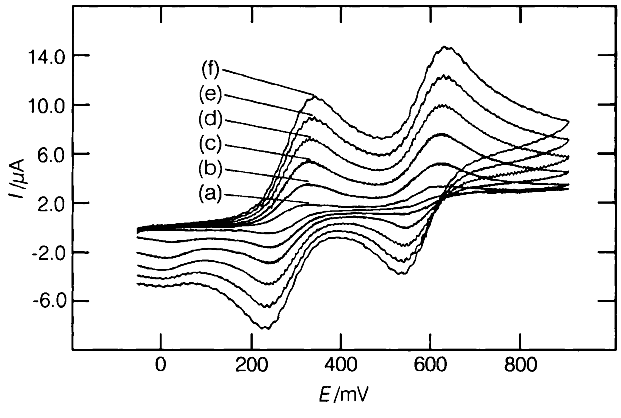


Fig. 1 Cyclic voltammogram of 2,6-dichloro-TMPD **11**; voltage scan rate *v*: 25 (a), 100 (b), 225 (c), 400 (d), 625 (e) and 900 mV s^{-1} (f) (*E vs.* ferrocene, anodic current plotted upwards).

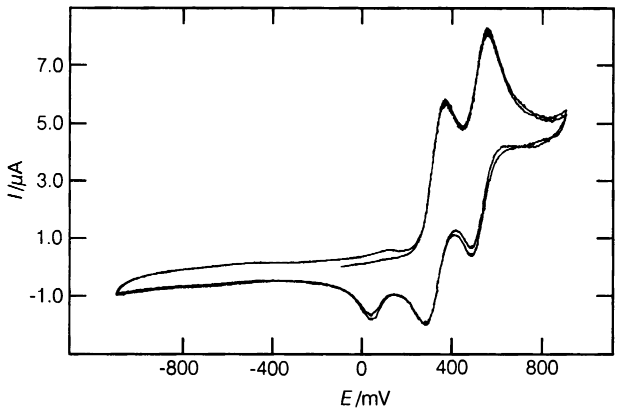


Fig. 2 Cyclic voltammogram of 2,6-dibromo-TMPD **8**; voltage scan rate *v*: 100 mV s^{-1} (*E vs.* ferrocene, anodic current plotted upwards).

shown in eqn. (1). However, the peak currents of the corresponding cathodic peaks shown in Fig. 1 are slightly smaller than those of the anodic reaction, in particular for slow voltage scan rates *v*. Furthermore, an additional reduction peak was observed at approx. 10 mV *vs.* ferrocene. This implies a chemical side reaction after the oxidation of compound **11** to **11**$^{2+}$. It is important to note that completely reversible electrochemical behaviour was found in CV-experiments where only the first oxidation step of compound **11** was scanned. In this case, the ratio of the observed anodic (i_p^a) to cathodic peak currents was close to one and the ratio of $i_p^a/v^{1/2}$ was constant (investigated range of $v = 25$ to 900 mV s^{-1}). Therefore, the chemical reaction definitely starts after the removal of the second electron (EECE-mechanism; E = electron transfer reaction, C = chemical reaction).

The dibromo-derivative **8** exhibited rather similar electrochemical properties. As example a complete cyclic voltammogram is reproduced in Fig. 2. Two oxidation peaks were observed, the peak currents of the corresponding reduction steps were again smaller and a third reduction peak occurred at 42 mV *vs.* ferrocene. During the next scan a new oxidation peak with a rather small peak current was found at approx. 113 mV. Thus, a new electrochemically active species had formed during the first scan. In analogy to compound **11** an EECE-mechanism is more reasonable for the explanation than an ECE-mechanism. The half wave potential of the new species generated during the CV experiment of compound **8** was approx. 78 mV. It is obvious that the accuracy of this value is limited due to the very small anodic peak current observed. Nevertheless, the value is very close to the first half wave potential of the monobromo-derivative **10** (54 mV *vs.* ferrocene, see Table 1). Compound **10** exhibited completely reversible electrochemical properties. Therefore, a possible explanation for the chemical side reaction observed in the CV experiments of 2,6-dibromo-TMPD **8** is an elimination reaction including one bromine atom. Since 2,6-dichloro-TMPD **11** showed comparable electrochemical behaviour, a reaction including the elimination of one chlorine atom is expected to be the explanation in this case.

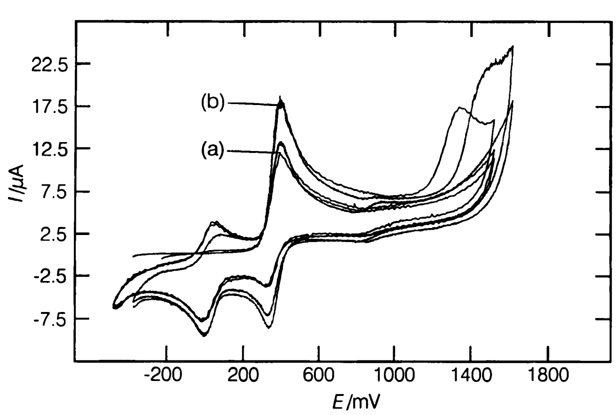


Fig. 3 Cyclic voltammogram of 2,6-diiodo-TMPD **9**; voltage scan rate *v*: 250 mV s^{-1} (a) and 500 mV s^{-1} (b) (*E vs.* ferrocene, anodic current plotted upwards).

In contrast to the dichloro- and dibromo-derivatives, the diiodo-compound **9** showed only one oxidation peak during the first scan (Fig. 3). In comparison to the measurements discussed above, the corresponding anodic peak current was generally very high, also when only a small potential window around the redox events was scanned. This indicates an EE-mechanism, where the second electron transfer is energetically equal or lower than the first one. Consequently only the dication **9**$^{2+}$ was observed. The corresponding cathodic peak current was clearly smaller than the anodic. Decreasing the scan rate also led to a comparably smaller reduction peak current; this also indicates a chemical side reaction. A second cathodic peak was observed and—in a second scan—the corresponding anodic peak. This again implies the development of a new electrochemically active species. In analogy to the CV results obtained for the compounds **8** and **10**, the corresponding monoiodo-derivative is expected. In addition it has to be mentioned that the increase/decrease of current at about 800 mV shown in Fig. 3 was caused by instrumental parameters.

Table 1 Measured half wave potentials, $E_{1/2}$, and potential difference between the two oxidation steps, ΔE (all potentials *vs.* ferrocene)

Compound	$E_{1/2}^1$/V	$E_{1/2}^2$/V	$E_{1/2}^{1+2}$/V	ΔE/V
8	0.328	0.527	—	0.20
9	—	—	0.365	—
10	0.054	0.425	—	0.37
11	0.286	0.585	—	0.30
12	0.363	0.840	—	0.48
13	0.077	0.420	—	0.34

The voltammograms of the products **12** and **13** showed completely reversible electrochemical behaviour (see Fig. 4 for compound **13**). The electrochemical data for the products **12** and **13** are collected in Table 1.

Comparison of electrochemical properties

In Table 1 the half wave potentials of the oxidation to the corresponding radical cations and dications, $E_{1/2}^1$ and $E_{1/2}^2$, respectively, are collected. Additionally, the differences of these potentials $\Delta E = E_{1/2}^1 - E_{1/2}^2$ are listed. All potentials are given *vs.* ferrocene. Comparing the 2,6-disubstituted TMPDs carrying different halogens it is obvious that the first redox activity correlates to the ordering number of the halogen. $E_{1/2}^1$

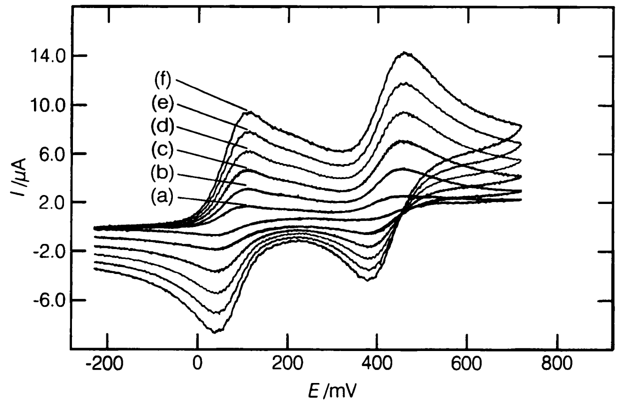


Fig. 4 Cyclic voltammogram of 2,6-bis(trimethylsilylethynyl)-TMPD **13**; voltage scan rate *v*: 25 (a), 100 (b), 225 (c), 400 (d), 625 (e) and 900 mV s^{-1} (f) (*E vs.* ferrocene, anodic current plotted upwards).

of 2,6-dichloro-TMPD **11** was 0.286 V, $E_{1/2}{}^{1} = 0.328$ V was found for the dibromo-derivative **8** and $E_{1/2}{}^{1+2} = 0.365$ V for 2,6-diiodo-TMPD **9**. While the first and second oxidation steps were separated by $\Delta E = 0.30$ V in the case of the dichloro-compound **11**, a reduced value of $\Delta E = 0.20$ V was found for 2,6-dibromo-TMPD **8**. The reduction of the ΔE value with increasing ordering number, and consequently further decreasing electronegativity and inductive effect, continued for 2,6-diiodo-TMPD **9** where immediate oxidation to the dication was observed. On the other hand, 2,6-dicyano-TMPD **12**, a derivative containing the pseudo-halogen groups CN as substituents, exhibited completely reversible electrochemical behaviour with $\Delta E = 0.48$ V. For the halogenated compounds a chemical instability was found after oxidation to the dication (see discussion above). In accordance with the general reactivity of halogenated hydrocarbons, the importance of the side reaction increased in the order $Cl < Br < I$ as can be deduced from the CV data (Fig. 1–Fig. 3). However, kinetic studies were not performed since this was not the aim of this work. Nevertheless, the results imply that, under appropriate conditions 2,6-dichloro-TMPD **11** and, especially, 2,6-dicyano-TMPD **12** could give stable radical cations and consequently be used as building blocks for molecular magnets. The derivatives **8** and, in particular, **9** should preferably be used as precursors to other *p*-phenylenediamines.

An interesting fact, especially with respect to conjugated polyradicals, is that 2,6-bis(trimethylsilylethynyl)-TMPD **13** showed reversible electrochemical behaviour. Heck reactions using precursor **9** together with other appropriate reactants (spin coupling units) seem to be a promising approach towards new magnetically active systems.

Conclusions

The aim of this investigation was the preparation of 2,6-disubstituted *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamines that can be used as precursors/building blocks for molecular magnets. 2,6-Dibromo-TMPD **8** and 2,6-diiodo-TMPD **9** could be successfully synthesised. In particular compound **9** can be used as precursor to other interesting derivatives. For example, the corresponding dichloro- and dicyano-derivatives, **11** and **12**, respectively, could be obtained. A more important result is that compound **9** could be used as reactant for Heck type reactions as shown with the preparation of 2,6-bis(trimethylsilylethynyl)-TMPD **13**. This is a promising result concerning the synthesis of corresponding conjugated polyradicals (*e.g.* oxidative coupling of terminal ethynyl groups after removal of the $Si(CH_3)_3$ protecting groups of product **13**, Heck reactions of compound **9** with other spin coupling units). Already the neutral polymers might be interesting, *e.g.* as a new material for hole transport layers in light emitting devices.

However, for molecular magnets the crucial factors are the formation and the stability of unpaired spins—in the case of 2,6-disubstituted TMPDs the corresponding radical cations. According to cyclic voltammetry, this should be possible for 2,6-dicyano-TMPD **12** and 2,6-bis(trimethylsilylethynyl)-TMPD **13**. Thus, the 2,6-disubstituted *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine motive is a promising building block for molecular magnets (charge-transfer complexes, polyradicals and so on).

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