Synthesis and crystallography of 8-halonaphthalene-1-carbonitriles and naphthalene-1,8-dicarbonitrile

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A convenient and high-yielding three-step synthesis of 8-halonaphthalene-1-carbonitriles has been achieved by ring opening of 1*H*-naphtho[1,8-*de*][1,2,3]triazine with the corresponding halides as the key step. Naphthalene-1,8-dicarbonitrile also has been synthesised from 8-bromonaphthalene-1-carbonitrile via palladium-catalysed cyanation of the aryl bromide. The crystal structures of 8-chloronaphthalene-1-carbonitrile, the A polymorph of the bromo analogue, and naphthalene-1,8-dicarbonitrile are isomorphous with orthorhombic symmetry. The B polymorph of the bromo compound and the iodo analogue are also isomorphous, but with monoclinic symmetry. In all of the halo carbonitriles, the molecules are disordered with respect to the location of the halogen atoms and the nitrile groups. There are no intermolecular X…NC interactions in any of the solids.

Keywords: copper, Sandmeyer reaction, nitriles, ring opening, triazine

Approximately linear intermolecular interactions between aromatic nitrile groups and aromatic halogen atoms are well known.[1] With this in mind, the syntheses of 8-halonaphthalene-1-carbonitriles (halo = chloro, bromo, iodo) was undertaken with the expectation that planar dimers with two CN…X interactions might form (Fig. 1). Note that the CN and X groups would be pushed away from each other so that the CN…X interactions would only be approximately linear. The compounds were synthesised and the crystal structures determined.

8-Chloronaphthalene-1-carbonitrile (**3a**) has been made previously by Kalb[2] by diazotisation of 8-chloronaphthalen-1-amine, and by Gore *et al.*[3] by diazotisation of 8-aminonaphthalene-1-carbonitrile. Neither of the starting amines are commercially available. The synthesis of 8-bromonaphthalene-1-carbonitrile (**3b**) appears to be unreported. The synthesis of 8-iodonaphthalene-1-carbonitrile (**3c**) has been reported by Müller *et al.*[4] from benz[*c,d*]indol-2(1*H*)-one, in a multistep synthesis. Naphthalene-1,8-dicarbonitrile (**4**) has been prepared from less accessible starting materials, including 8-aminonaphthalene-1-sulfonic acid,[5] acenaphtho[1,2-*c*]furazan oxide,[6,7] acenaphtho[1,2-*c*]-1,2,5-thiadiazole 1,1-dioxide,[8] and acenaphthenequinone bistosylhydrazone.[9–11] Most of the methods are inconvenient or low-yielding and start from acenaphthenequinone, which is expensive.

Results and discussion

The key intermediate triazine **1** (Scheme 1) was prepared[12–14] by diazotisation of the commercially available naphthalene-1,8-diamine[15] with isoamyl nitrite in acetic acid and ethanol in 81% yield.

The next step is a Sandmeyer reaction of triazine **1** with conc HCl catalysed by copper turnings, which gave 8-chloronaphthalen-1-amine (**2a**) in 81% yield (Scheme 1).[16,17] The final step was a Sandmeyer reaction[18] with **2a**, which gave 8-chloronaphthalene-1-carbonitrile (**3a**) in 56% yield. Several experimental conditions were screened for the diazotisation of **2a** using HCl or AcOH, but reduction of the concentration of nucleophilic chloride ion seemed to be the key, since switching to sulfuric acid, followed by the usual mixture of cuprous chloride and sodium cyanide, gave **3a** in the best yield, 56%, as reported.

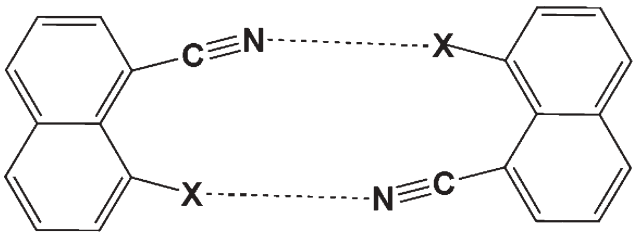

Fig. 1 Hypothesised planar dimer.

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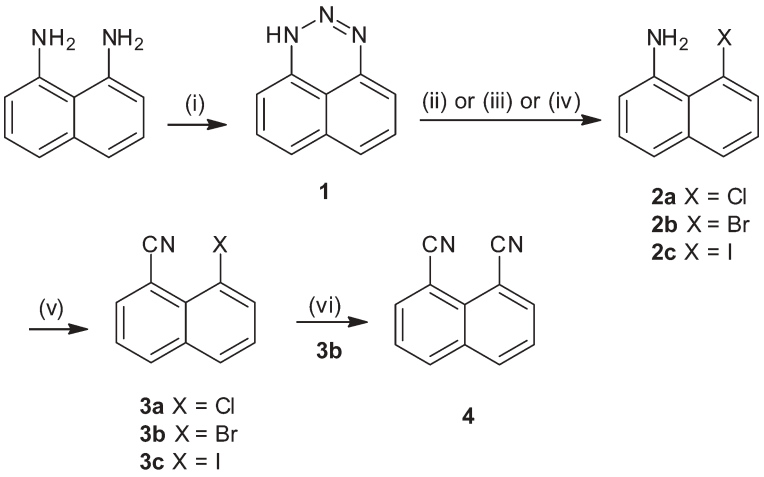
The synthesis of the 8-bromonaphthalene-1-carbonitrile (**3b**) and 8-iodonaphthalene-1-carbonitrile (**3c**) compounds followed the same sequences used for the 8-chloronaphthalene-1-carbonitrile (**3a**). Reaction of the triazine **1** with 48% HBr or 57% HI catalysed by copper turnings gave **2b** in 75% and **2c** in 54% yields, respectively. Diazotisation of **2b** and **2c** with sodium nitrite in aqueous sulfuric acid, followed by a Sandmeyer reaction with a mixture of cuprous chloride and sodium cyanide gave **3b** in 53% and **3c** in 49% yields, respectively.

The method of Weissman *et al.*[19] was used for the cyanation of aryl bromides with **3b** (1.0 mmol), $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.25 mmol), Na_2CO_3 (1.0 mmol), and $Pd(OAc)_2$ (0.01 mmol) in *N*,*N*-dimethylacetamide (5 mL) at 120 °C for 3 h, giving naphthalene-1,8-dicarbonitrile (**4**) in 81% yield (Scheme 1). In order to develop a shorter and effective synthesis for naphthalene-1,8-dicarbonitrile (**4**), 1,8-dibromonaphthalene (**5**) was prepared[20] by diazotisation of triazine **1** with sodium nitrite in sulfuric acid, followed by the addition of CuBr/HBr in 44% yield, and cyanation of the dibromide (**5**) by Weissman's method gave naphthalene-1,8-dicarbonitrile (**4**) in 78% yield (Scheme 2).

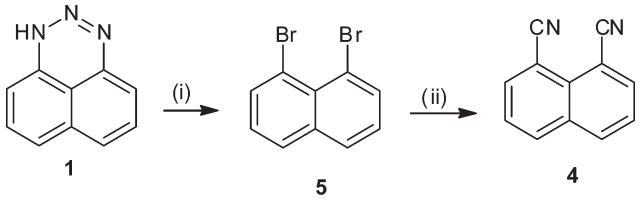
X-ray crystallography

For each of the compounds crystals were grown by room temperature evaporation from six different solvents. The A polymorph of the bromo compound was obtained from benzene, methylene chloride, and chloroform; the B polymorph from acetone, carbon tetrachloride, and acetonitrile. The chloro, iodo, and dicyano compounds gave the same crystalline form from all six of the solvents.

X-ray data were collected at 174 K on a Bruker SMART 1K CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved using the programs SMART and SAINT[21] and SHELXTL[22]. Hydrogen atoms were placed in idealized positions and constrained to ride on the parent C atom with $U_{iso}(H) = 1.2\ U_{eq}(C)$. The crystallographic coordinates have been deposited with the Cambridge Crystallographic Data Center; CCDC 815418–815422, which correspond to **3a**, **3bA**, **3bB**, **3c**, and **4**, respectively. CCDC is available free of charge via the Internet at www.ccdc.cam.ac.uk/datarequest/cif. Crystal data and refinement details are listed in Table 1.



Scheme 1 (i) Isoamyl nitrite, AcOH, EtOH, 81%; (ii) Cu, HCl, rt, 12h, 81%; (iii) Cu (10 mol%), HBr, rt,12h, 75%; (iv) Cu (10 mol%), HI, rt, 12h, 54%;(v) (a) $NaNO_2$, H_2O, H_2SO_4, 0 °C; (b) CuCl, NaCN, H_2O, 0 °C, rt, 2–3 h, 56% for **3a**, 53% for **3b** and 49% for **3c** (over two steps); (vi) 0.5 mol% $Pd(OAc)_2$,$K_4[Fe(CN)_6]$, Na_2CO_3, DMAC, 3 h, 120 °C, 81%.



Scheme 2 (i) $NaNO_2$, 6.9 M H_2SO_4, –5 °C, 2 h; (b) CuBr, 47% HBr, 85 °C, 1 h, 44%; (ii) 1 mol% Pd $(OAc)_2$, $K_4[Fe(CN)_6]$, Na_2CO_3, DMAC, 3 h, 120 °C, 78%.

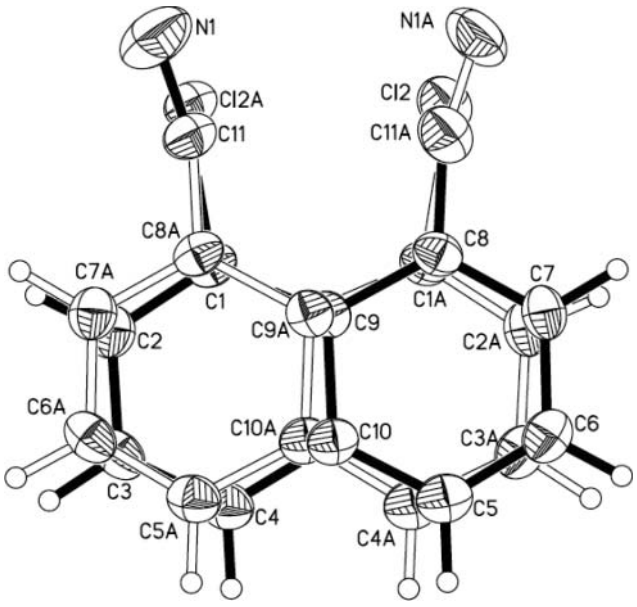


Fig. 2 8-Chloronaphthalene-1-carbonitrile (**3a**). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The disorder has C1, C2, etc. with 41.4(3)% occupancy; C1A, C2A, *etc.* with 58.6(3)% occupancy. The displacement ellipsoid diagrams for **3bA**, **3bB**, and **3c** look essentially the same. That is, they are all disordered with the X and CN groups changing places.

Anisotropic displacement ellipsoids and atom labeling are shown for (**3a**) and (**4**) in Figs 2 and 3. All of the structures except (**4**) show disorder about a two-fold (in **3bB** and **3c**) or a pseudo two-fold axis (**3a** and **3bA**).

There is no crystallographic two-fold axis in (**4**). (**3a**), (**3bA**) and (**4**) are isomorphous with orthorhombic symmetry. (**3bB**) and (**3c**) are also isomorphous but with monoclinic symmetry, although the monoclinic angles are very close to 90°. The structures of 1,8-dibromonaphthalene[23] and 1,8-diiodonaphthalene[24] are known, but they are not isomorphous with each other nor with any of the compounds described here. Figures 4 and 5 show the packing in (**3a**) and in (**3c**). It is not surprising to have disorder between the X and CN groups, since they are about the same size. However, given that X…NC intermolecular interactions are well known and increase in strength as X goes from Cl to I, it is surprising that in none of these structures are there any X…NC contacts. The packings in the two polymorphs show strong similarities. The differences can be seen in the two figures.

In summary, we report a general, short, and efficient procedure for synthesising 8-halonaphthalene-1-carbonitriles (**3a**, **3b**, and **3c**) by copper-catalysed halide-ion ring opening of the triazine **1**. Palladium-catalysed cyanation of the bromide (**3b**) as well as dibromide (**5**) gave naphthalene-1,8-dicarbonitrile (**4**).

Experimental

Melting points (uncorrected) were obtained on a Fisher-Johns melting point apparatus. The IR spectra were recorded with an M series FTIR instrument (Midac Corporation, California, USA). Column chromatography was performed on silica gel (200–300 mesh, purchased from Sorbent Technologies, USA). NMR spectra were recorded on a Bruker AV300 spectrometer. ^1H and ^{13}C NMR spectra were calibrated with TMS as an internal standard. The HRMS (ESI) spectra were obtained on a Bruker BioTOF II spectrometer in positive-ion mode. Elemental analyses were performed at M-H-W Laboratories, Phoenix, AZ. Triazine **1** was prepared by a literature procedure[12] and 1,8-dibromonaphthalene (**5**) was prepared by a literature procedure.[20]

8-Chloronaphthalen-1-amine (**2a**): 1*H*-Naphtho[1,8-*de*][1,2,3]triazine (**1**, 1.521 g, 9.00 mmol) was mixed with an excess of 36% hydrochloric acid (75 mL). Copper turnings (0.038 g) were added and the mixture was stirred overnight. The resulting mixture was diluted with water (200 mL) and heated at reflux for 30 min. The resulting almost clear aqueous solution was filtered, cooled, basified with aqueous ammonia (until blue to litmus paper), and extracted with ether (2 × 30 mL). The combined extracts were dried over Na_2SO_4 and the solvent was removed using a rotating evaporator and the product was purified by column chromatography (neutral alumina, hexane-EtOAc, 8:2), giving **2a** (1.24 g, 81%) as a colourless solid; m.p. 94–95 °C (lit.[25] 95–96 °C).

IR ($CHCl_3$, cm^{-1}): 3501, 3410, 3007, 1630, 1568. ^1H NMR (300 MHz, $CDCl_3$): δ 7.65 (d, J = 6.3 Hz, 1H), 7.38 (d, J = 6.3 Hz, 1H), 7.21–7.30

Table 1 Crystal data and structure refinement summary

Compound	**3a**(Cl/CN)	**3bA**-(Br/CN-A)	**3bB**-(Br/CN-B)	**3c**-(I/CN)	**4**-(CN/CN)
Chemical formula	$C_{11}H_6ClN$	$C_{11}H_6BrN$	$C_{11}H_6BrN$	$C_{11}H_6IN$	$C_{12}H_6N_2$
Mr	187.62	232.08	232.08	279.07	178.19
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	I2/a	I2/a	$P2_12_12_1$
a(Å)	3.8403(10)	3.8698(11)	7.3311(15)	7.3871(15)	3.8146(6)
b(Å)	7.815(2)	7.859(2)	8.6054(17)	8.8191(18)	7.9790(11)
c(Å)	28.368(8)	28.788(8)	13.992(3)	14.171(3)	28.128(4)
β(°)	90	90	90.02(3)	90.10(3)	90
V(Å^3)	851.4(4)	875.5(4)	882.7(3)	923.2(3)	856.1(2)
Z	4	4	4	4	4
μ(mm^{-1})	0.39	4.64	4.60	3.41	0.09
h range	–4,4	–5,5	–9,9	–9,9	–4,4
k range	–10,10	–10,10	–11,11	–11,11	–10,10
l range	–36,36	–37,37	–18,17	–18,18	–36,35
meas. Refl.	9617	9879	4984	6631	100001
uniq. Refl.	1934	1988	1016	1054	1204
obs. refl.	1480	1597	928	978	1144
R^1	0.059	0.049	0.062	0.062	0.042
wR^2	0.101	0.084	0.168	0.154	0.108
Largest diff.	0.19	0.37	0.71	0.89	0.18
Peak and hole (e/Å^3)	–0.19	–0.42	–0.79	–0.50	–0.22
CCDC #	815418	815419	815420	815421	815422

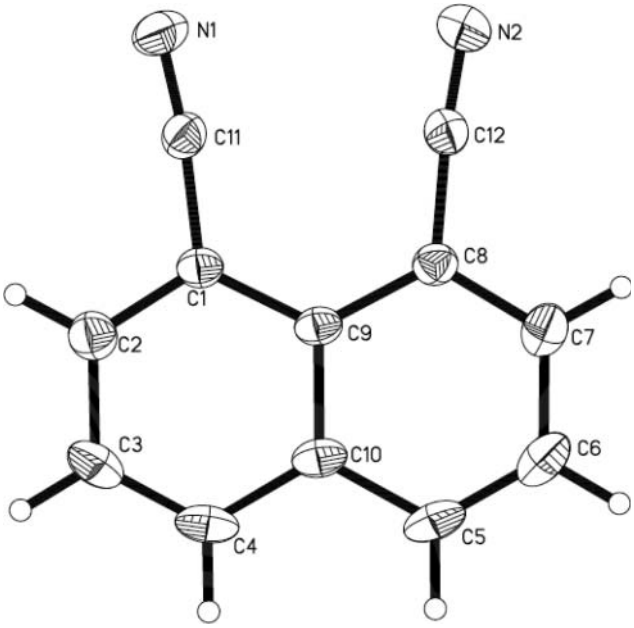


Fig. 3 Naphthalene-1,8-dicarbonitrile (**4**). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The molecule does not lie on a two-fold axis.

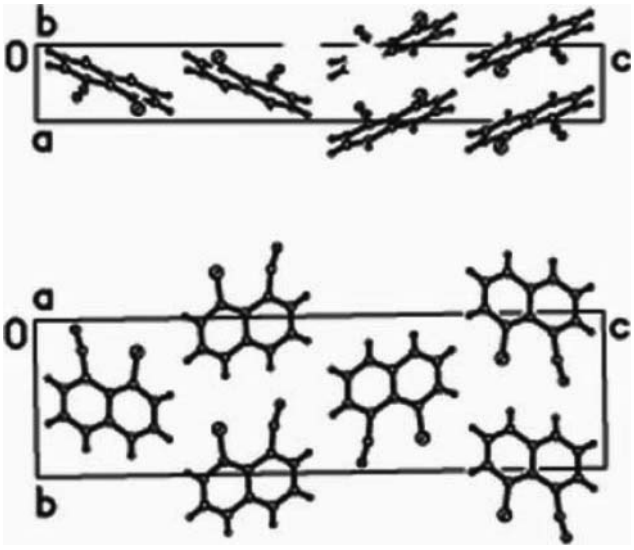


Fig. 4 Packing in 8-chloro-1-naphthalenenitrile. Top: view along the b axis. Bottom: view along the a axis. Only one of the two disordered orientations of the molecules is shown to improve the clarity.

(m, 3H), 6.72 (dd, *J* = 6.9 Hz, 2.1 Hz, 1H), 5.19 (br s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.9, 137.5, 128.5, 128.4, 127.7, 127.6, 127.3, 125.41, 118.9, 112.3. HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{10}H_8ClN$: 200.0243; found 200.0249.

8-Bromonaphthalen-1-amine (**2b**): 1*H*-Naphtho[1,8-*de*][1,2,3]triazine (0.507 g, 3.00 mmol) was added to an excess of 48% hydrobromic acid (20 mL). Copper turnings (0.038 g) were added and the mixture was stirred overnight. The resulting mixture was diluted with water (200 mL) and heated at reflux for 30 min. The resulting almost clear aqueous solution was filtered, cooled, basified with aqueous ammonia (until blue to litmus paper), and extracted with ether (2 × 30 mL). The combined extracts were dried over Na_2SO_4 and the solvent was removed using a rotating evaporator and the product was purified by column chromatography (neutral alumina, hexane-EtOAc, 8:2), giving **2b** (0.50 g, 75%) as a colourless solid; m.p. 87–88 °C (lit.[26] 87–88 °C). IR ($CHCl_3$, cm^{-1}): 3490, 3400, 1616, 1563. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (d, *J* = 9.5 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.15–7.30 (m, 3H), 6.75 (dd, *J* = 8.6, 2.3 Hz, 1H), 5.21 (br s, 2NH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.6, 140.2, 136.6, 129.9, 126.7, 126.2, 122.5, 119.9, 112.6, 87.3. HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{10}H_8BrN$: 243.9738; found: 243.9736.

8-Iodonaphthalen-1-amine (**2c**): 1*H*-Naphtho[1,8-*de*][1,2,3]triazine (0.507 g, 3.00 mmol) was mixed with an excess of hydroiodic acid (20 mL). Copper turnings (0.019 g) were added and the mixture was stirred overnight. The resulting mixture was diluted with water (70 mL) and heated at reflux for 30 min. The resulting almost clear aqueous solution was filtered, cooled, basified with aqueous ammonia (until blue to litmus paper), and extracted with ether (2 × 15 mL). The combined extracts were dried over Na_2SO_4 and the solvent was removed using a rotating evaporator. The brown solid was purified by column chromatography (neutral alumina, hexane–EtOAc, 8:2), giving **2c** (0.43 g, 54%) as a light yellow solid; m.p. 79–80 °C (lit.[27] 79–80 °C).

IR ($CHCl_3$, cm^{-1}): 3480, 3388, 1620, 1558. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.73 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.25–7.31 (m, 2H), 6.97 (dd, *J* = 7.5 Hz, 7.2 Hz, 1H), 6.80 (dd, *J* = 8.6, 2.3 Hz, 1H), 5.01 (br s, 2NH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.6,

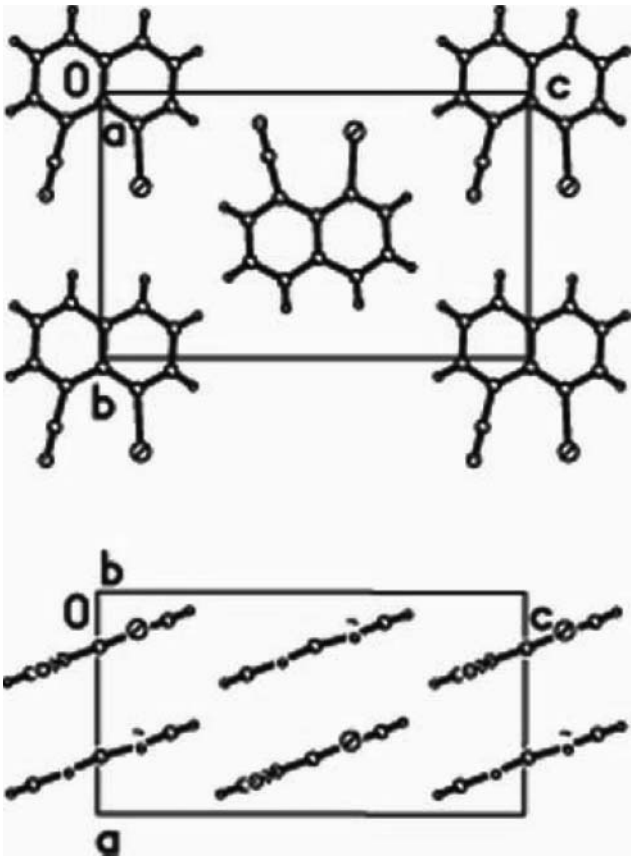


Fig. 5 Packing in 8-iodonaphthalene-1-carbonitrile. Top: view along the *a* axis. Bottom: view along the *b* axis. Only one of the two disordered orientations of the molecules is shown to improve the clarity.

140.2, 136.6, 129.9, 126.7, 126.2, 122.5, 119.9, 112.6, 87.3. HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{10}H_8IN$: 291.9599; found: 291.9594.

*Synthesis of compounds (**3**); general procedure*

A. Cuprous cyanide solution was prepared by adding a solution of sodium cyanide (0.826 g, 16.80 mmol) in water (6.0 mL) to a stirred solution of cuprous chloride (0.668 g, 6.75 mmol) in water (10 mL) at 0 °C.

B. H_2SO_4 (0.242 mL) was added to a mixture of **2** (4.50 mmol) and water (5 mL) at 0 °C, and the solution was stirred for 20 min. This solution was kept at 0 °C while a solution of $NaNO_2$ (0.345 g, 5.00 mmol) in water (5 mL) was added. The solution turned orange and gas bubbles were evolved. The cooled cuprous cyanide solution from part A was added and the mixture was stirred for 2 h at room temperature and warmed to 50 °C with stirring for 2 h and then cooled to room temperature. The solution was extracted with ethyl acetate (2 × 20 mL), washed with aqueous 5% $NaHCO_3$ (20 mL) and dried over Na_2SO_4. The solvent was removed using a rotating evaporator, giving a crude product which was purified by column chromatography (silica gel, hexane-EtOAc, 8:2), giving the desired compounds **3**.

8-Chloronaphthalene-1-carbonitrile (**3a**): Colourless solid, 56% yield, m.p. 144–145 °C (lit.[3] 145 °C). IR ($CHCl_3$ cm^{-1}): 3019, 2222 (CN), 1506, 1215, 823, 763. ^{1}H NMR (75 MHz, $CDCl_3$): δ 8.12–8.06 (m, 2H), 7.85 (d, *J* = 7.2 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.62–7.48 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.7, 134.9, 134.0, 130.3, 128.7, 128.4, 127.1, 125.4, 119.4 (CN), 108.0. HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{11}H_6ClN$: 210.0086; found: 210.0079.

8-Bromonaphthalene-1-carbonitrile (**3b**): Colourless solid, 53% yield, m.p. 133–135 °C. IR ($CHCl_3$, cm^{-1}): 2253 (CN), 1500, 1261, 1203, 908, 736. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.96 (d, *J* = 7.5 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.57 (t, *J* = 8.1 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.2, 134.9, 134.6, 134.3, 129.5, 129.1, 127.5, 125.3, 119.3 (CN), 109.5. HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{11}H_6BrN$ 253.9581; found: 253.9580. Anal. Calcd for $C_{11}H_6BrN$: C, 56.93; H, 2.61; Br, 34.43; N, 6.04. Found: C, 56.89; H, 2.58; Br, 34.39; N, 6.10%.

8-Iodonaphthalene-1-carbonitrile (**3c**): Colourless solid, 49% yield, m.p. 116–117 °C (lit.[4] 113–115 °C). IR ($CHCl_3$, cm^{-1}): 3019, 2216 (CN), 1497, 1261, 1215, 820, 768. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.35 (dd, *J* = 7.5, 1.2 Hz, 1H), 8.11–8.05 (m, 2H), 7.92 (dd, *J* = 8.4, 1,4 Hz, 1H), 7.55 (t, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 8.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.4, 138.7, 134.9, 134.5, 131.3, 130.2, 128.0, 125.2, 118.8 (CN), 112.4, 92.2. HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{11}H_6IN$: 301.9443, found 301.9438.

Naphthalene-1,8-dicarbonitrile (**4**): Bromide **3b** (0.232 g, 1.00 mmol), DMAC (5 mL), $K_4[Fe(CN)_6]\cdot 3H_2O$ (0.105 g, 0.250 mmol), sodium carbonate (0.106 g, 1.00 mmol) and $Pd(OAc)_2$ (0.0033 g, 0.010 mmol) were placed in a 25-mL flask. The flask was evacuated, filled with nitrogen, and heated at 120 °C for 3 h. Upon completion (TLC), the mixture was cooled to room temperature and diluted with EtOAc (10 mL). The resulting slurry was filtered and the filtrate was washed with water (2 × 15 mL) and 5% NH_3 in water (10 mL). The organic layer was dried over Na_2SO_4 and the solvent was removed using a rotating evaporator, giving a light yellow solid, which was purified by column chromatography (silica gel, hexane-EtOAc, 7:3), giving **4** (0.145 g, 81%) as a colourless solid; m.p. 231–232 °C (lit.[5] 232 °C). IR ($CHCl_3$, cm^{-1}): 2283 (CN), 1586, 1360, 930, 743. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.5 Hz, 2H), 8.17 (d, *J* = 7.5 Hz, 2H), 7.71 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.7, 134.4, 133.2, 126.6, 116.6 (CN), 108.6, 104.8. HRMS (ESI): *m/z* [M + Na]$^+$ calcd for $C_{12}H_6N_2$: 201.0429; found: 201.0425.

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