Multisubstituted phthalonitriles, naphthalenedicarbonitriles, and phenanthrenetetracarbonitriles as precursors for phthalocyanine syntheses

Clifford C. Leznoff, Dmitri S. Terekhov, Colin R. McArthur, Steven Vigh, and Jing Li

Abstract: Electrophilic aromatic nitration under mild conditions of 4-hydroxypythalonitrile gave 4-hydroxy-3-nitrophthalonitrile and 4-hydroxy-5-nitrophthalonitrile, while bromination yielded 3-bromo-4-hydroxypythalonitrile, 4-bromo-5-hydroxypythalonitrile, and 3,5-dibromo-4-hydroxypythalonitrile. Iodination gave 4-hydroxy-5-iodophthalonitrile and 4-hydroxy-3,5-diodophthalonitrile. Coupling of 4-iodophthalonitrile, 3-iodophthalonitrile, and 5-iodo-2,3-dicyanonaphthalene with trans-1,2-bis(tri-n-butylstannyl)ethene gave trans-1,2-bis(3,4-dicyanophenyl)ethene, trans-1,2-bis(2,3-dicyanophenyl)ethene, and trans-1,2-bis(6,7-dicyanonaphthyl)ethene. Photocyclization of a dilute solution of cis- or trans-1,2-bis(3,4-dicyanophenyl)ethene in dioxane gave a 1:1 mixture of 2,3,6,7- and 2,3,5,6-tetracyanophenanthenes separable by chromatography. Key words: phthalonitriles, naphthalenedicarbonitriles, phenanthrenetetracarbonitriles, electrophilic substitution.

Résumé : La nitration électrophile aromatique du 4-hydroxypythalonitrile, dans des conditions douces, conduit au 4-hydroxy-3-nitrophthalonitrile et au 4-hydroxy-5-nitrophthalonitrile alors que sa bromation fournit du 3-bromo-4-hydroxypythalonitrile, du 4-bromo-5-hydroxypythalonitrile, et du 3,5-dibromo-4-hydroxypythalonitrile. L’iodation fournit du 4-hydroxy-5-iodophthalonitrile et du 4-hydroxy-3,5-diodophthalonitrile. Le couplage des 4-iodophthalonitrile, 3-iodophthalonitrile et 5-iodo-2,3-dicyanonaphthalène avec du trans-1,2-bis(tri-n-butylstannyl)éthène fournit du trans-1,2-bis(3,4-dicyanophényl)éthène, du trans-1,2-bis(2,3-dicyanophényl)éthène et du trans-1,2-bis(6,7-dicyanonaphthyl)éthène. La photocyclisation d’une solution diluée des isomères cis- et trans-1,2-bis(3,4-dicyanophényl)éthène dans le dioxane fournit un mélange 1 : 1 des 2,3,6,7- et 2,3,5,6-tétracyanophenanthenes que l’on peut séparer par chromatographie. Mots clés : phthalonitriles, naphthalènedicarbonitriles, phénanthrenétetracarbonitriles, substitution électrophile.

[Traduit par la rédaction]

Some substituted aromatic o-dinitriles are widely used in the synthesis of phthalocyanines (1), polymers, and intermediates in organic syntheses (2). Most common methods of their synthesis include cyanoation of aromatic halides (2) or more recently triflates (3), nucleophilic substitution of nitrophthalonitriles (4–6), aromatic coupling using, for example, 4-iodophthalonitriles mediated by palladium catalysts (7, 8), Diels–Alder addition of fumaronitrile or dicyanoacetylene to substituted dienes and furans (9), and multistep synthesis involving the transformation of aromatic o-diacids via imides and diimides (10) to dinitriles (11–13). Direct electrophilic aromatic substitution of aromatic o-dinitriles is generally not used owing to the presence of the two deactivating electron-withdrawing nitrile groups and the fact that these groups are susceptible to hydrolysis during the strongly acidic conditions of these reactions. Our interests in phthalocyanine synthesis led us to prepare a variety of multisubstituted phthalonitriles, bisaromatic o-dinitriles, naphthalenedicarbonitriles (5-substituted-2,3-dicyanonaphthalenes), and phenanthrenetetracarbonitriles, using a wide variety of methods including rarely used electrophilic aromatic substitution reactions and photocyclization.

Iodination, nitration, and bromination of 4-hydroxypythalonitrile (1)

A recent paper by Gaude et al. (14) described the direct iodination of phenols by iodine nitrate and we thought that this procedure could be successful in the direct iodination of 4-hydroxypythalonitrile (1)(15) as the two nitrile groups may not sufficiently deactivate phenol 1 towards electrophilic aromatic substitution. Thus, treatment of 1 with iodine nitrate in acetonitrile for 2 h at room temperature gave a mixture, separable by flash chromatography, of 4-hydroxy-3,5-diodophthalonitrile (2) and 4-hydroxy-5-iodophthalonitrile (3) in 5 and 2.5% yield, respectively (Scheme 1).

The poor yields of 2 and 3 (probably as a result of the electron-deactivating cyano groups of 1) and the possibility of converting nitro groups into diazonium salts and iodo groups

C.C. Leznoff,1 D.S. Terekhov, C.R. McArthur, S. Vigh, and J. Li. Department of Chemistry, York University, North York (Toronto), ON M3J 1P3, Canada.

1 Author to whom correspondence may be addressed.
Bromination (9) of 2,3-dimethyl-1-nitrobenzene (20) gave 2-bromomethyl-3-dibromoethyl-1-nitrobenzene (21), which on treatment (9) with sodium iodide in N,N-dimethylaniline and fumaronitrile (22) yielded the known 5-iodo-2,3-dicyanophenylacene (23), prepared by a different route (26). Reduction of 23 (26), gave 5-amino-2,3-dicyanophenylacene (24) (26), which upon diazoniation and treatment with potassium iodide gave the unknown 5-iodophenacyl-2,3-dicyanophenylacene (25). Coupling of 25 with 16 gave trans-1,2-bis(6,7-dicyano-4-hydroxyphthalonitrile (6) and a mixture of monobromo-4-hydroxyphthalonitrile (7) and 2,3-dibromo-2,4-dicyanophenylacene (26) (Scheme 4). The mixture of 4 and 5 was treated with diazomethane to give the less polar 4-methoxy-4-nitrophthalonitrile (9) and 4-methoxy-3-nitrophthalonitrile (10), while the mixture of 7 and 8 was alkylated using K₂CO₃ and l-bromobutane to give 4-bromo-5-butoxyphthalonitrile (11) and 3-bromo-4-butoxyphthalonitrile (12) in 30 and 34% overall yield from 1, respectively (Scheme 1).

Bisdicyanoarylene from dicyanooiodoarenes
Catalytic reduction of 3-nitrophthalonitrile (13) (21) with a poisoned palladium catalyst (22) gave 3-aminophthalonitrile (14) in 55–83% yields, which are considerably higher than previously reported (23). Diazotization of 14 and treatment of the diazonium salt with potassium iodide gave 3-iodophthalonitrile (15), only mentioned in an article but not characterized (24). Coupling of 15 with trans-1,2-bis(tri-n-butylstannyl)ethene (16) (25) gave trans-1,2-bis(2,3-dicyanophenyl)ethene (17) in 59% yield. In an attempt to prepare the cis isomer of 17, iodo 15 was coupled with acetylene and a palladium catalyst (7, 8) to give 1,2-bis(2,3-dicyanophenyl)ethene (18). Catalytic hydrogenation of 18 over a Lindlar catalyst as previously described did not result in semi-hydrogenation and only starting material was recovered. Hydrogenation over palladium on charcoal afforded the fully saturated 1,2-bis(2,3-dicyanophenyl)ethene (19) (Scheme 2).

Since the yields of 4 and 5 were still unsatisfactory, we decided to try a rarely used brominating agent, N,N-dibromoisoocyanuric (NBI) acid (19, 20) known to brominate aromatic compounds containing both activating and deactivating substituents. Although sulfuric acid is used in this procedure, the reaction time is short and the temperature low. Hence, 1 was reacted with NBI in concentrated sulfuric acid for 10 min at room temperature to give 3,5-dibromo-4-

led us to consider direct nitration of 1, using the mild nitrat-
arylenes 17 and 26 were extremely insoluble compounds, which likely caused attempts at subsequent reactions to fail. In an attempt to make a more soluble cis isomer of 26, compound 25 was coupled with acetylene in the presence of copper iodide and bis(triphenylphosphine)palladium dichloride (7, 8) to give 1,2-bis(6,7-dicyanonaphthyl) ethyne (27) in 54% yield (Scheme 3). This highly insoluble compound also proved resistant to semi-hydrogenation.

2,3,6,7-Tetracyanophenanthrene (31) and 2,3,5,6-tetracyanophenanthrene (32)
Attempts to induce photocyclization (27–29) of 17 and 26 to give exclusively one isomer of tetracyanoarenes failed, probably because of their extreme insolubility. In a search for more soluble precursors, 4-iodophthalonitrile (28) (8) was coupled with 16 to give trans-1,2-bis(3,4-dicyanophenyl) ethyne (29) in 94% yield. The cis isomer (30) has previously been made in our laboratory (26). Although 29 and 30 were both highly insoluble in most solvents, photocyclization of 29 and 30 was effected in a dilute solution of dioxane to afford a 1:1 mixture of 2,3,6,7-tetracyanophenanthrene (31) and 2,3,5,6-tetracyanophenanthrene (32) in 60–75% yield (Scheme 4). Regioselectivity in stilbene-like photocyclization reactions can vary, depending on the substituent (30).

The separation of this mixture was finally achieved using flash chromatography and slow elution with ethyl acetate–hexane (1:3) over 12 days to give pure 31 and 32. A third possible isomer, namely 3,4,5,6-tetracyanophenanthrene, was not detected in any of the photocyclization experiments.

Spectroscopic analysis
All nitriles exhibited typical nitrile absorption at 2220–2240 cm⁻¹ in their infrared spectra. The NMR spectra of all compounds were consistent with their structures. The structure of the tribromo derivative 21, however, was determined by the fact that long-range coupling occurred between the proton at C-4 and the CHBr₂ group to give a doublet of doublets (see Experimental), and hence the CHBr₂ group is at the 3 position.

A NOESY spectrum of compound 25 exhibited long-range coupling between the singlet at 8.88 ppm (H-C1) and the doublet at 8.20 ppm (H-C8). Thus, the other singlet at 8.61 ppm is H-C4, the doublet at 8.49 is H-C6, and the triplet at 7.62 is H-C7. The HH-COSY and NOESY spectra of 32 (Figs. 1 and 2) clearly exhibited a singlet at 9.03 ppm (H-C1) coupled to a doublet at 8.31 ppm (H-C10), while the singlet at 10.03 ppm is uncoupled and is ascribed to H-C9, which shows long-range coupling to H-C8 at 8.65 ppm, leaving the remaining doublet at 8.47 ppm for H-C7. All new compounds exhibited parent ions in their mass spectra and satisfactory elementary analysis or high-resolution mass spectra (HRMS).

The ready availability of multisubstituted phthalonitriles, biphenanthro- and tetracyanophenanthrenes will enable the preparation of unusual phthalocyanines.

Experimental
Matheson high-purity argon was used to maintain inert atmosphere conditions. Infrared (IR) spectra were recorded on a Pye Unicam SP1000 infrared spectrophotometer using KBr discs. Nuclear magnetic resonance (NMR) spectra for proton and carbon were recorded on a Bruker AM300 NMR spectrometer unless otherwise stated. TMS was used as the internal standard. The positions of the signals are reported in δ units. The splittings of the signal are described as singlets (s), doublets (d), triplets (t), quartets (q), pentets (p), hexets (h) doublets of doublets (dd), broad (br), or multiplets (m). The ultraviolet–visible spectra (UV–VIS) were recorded on a Varian CARY 2400 spectrophotometer UV–VIS–NIR. Mass spectra (MS) were recorded at 70 eV using a VG Micromass 16F mass spectrometer for molecules less than 900 amu or a Kratos Profile in the EI mode. The number in parentheses after the indicated ion shows the percentage of the base peak represented by that ion. The high-resolution mass spectra (HRMS) were obtained at 70 eV of a DEI model using a ZAB-E double focusing spectrometer of BE geometry. Melting points (mp) were determined using a Kofer hot stage melting point apparatus and are uncorrected. Flash chromatography was performed using silica gel of particle size 20–45 μm. All reactions were stirred with a magnetic stirrer. Ultrasound activation was carried out using a Branson 1200 sonicator. All
solvents were freshly distilled before use. Microanalysis were performed by Guelph Chemical Laboratory Ltd., Guelph, Ontario. Thin-layer chromatography (TLC) was performed using silica gel G as the absorbent.

4-Hydroxy-3,5-diiodophthalonitrile (2) and 4-hydroxy-5-
iodophthalonitrile (3)
Silver nitrate (0.85 g, 5 mmol) in 15 mL of acetonitrile was added dropwise to a solution containing 1.27 g of iodine (5 mmol) in 30 mL of acetonitrile, while the solution was stirred at 0°C. After 5 min, the precipitate of silver iodide (about 2.5 mmol) was filtered off and then compound 1 (0.72 g, 5 mmol) in 10 mL of acetonitrile was added to the filtrate. The resulting solution was stirred at room temperature for 2 h. An additional precipitate of silver iodide (about 2.5 mmol) was filtered off. The filtrate was washed with a solution of sodium bisulfite. The organic layer was dried over anhydrous magnesium sulfate for 2 h. The crude product was chromatographed on silica gel with petroleum ether and toluene (1:1). The first fraction gave a small amount of a yellow band. The second fraction was collected to give, in 5% yield, 70 mg of compound 3; mp 237–239°C; IR (KBr, cm⁻¹): 3320 (OH), 3070, 2950, 2900, 2850, 2230 (CN), 1570, 1550, 1480, 1330, 1170, 1120, 900; ¹H NMR (DMSO-d₆) δ: 9.50 (s, 1H, OIf), 8.52 (s, 1H, H-C₆ or l₁-C₃), 8.48 (s, 1H, I₁-C₃ or F₁-C₆); MS m/z: 210 (M⁺, 100). Exact Mass calcd. for C₃H₃N₂IO: 269.9289; found: 269.9289. Further elution gave, in 2–3% yield, 52 mg of compound 2; mp 290°C (dec.); IR (KBr, cm⁻¹): 3360(O-H), 2240(C=N), 1550, 1552, 1440, 1380, 1302, 1240, 1130, 920; ¹H NMR (DMSO-d₆) δ: 8.43 (s, 1H, H-C₆), 4.3 (br, s, 1H, OH). Exact Mass calcd. for C₅H₃N₃I₂O: 395.8255; found: 395.8255.
Fig. 2. The $^1$H-$^1$H NOESY NMR spectrum of 2,3,5,6-tetrayanophenanthrene (32) in DMSO-$d_6$.

4-Hydroxy-5-nitrophthalonitrile (4) and 4-hydroxy-3-nitrophthalonitrile (5)
To a 50 mL round-bottomed flask, compound 1 (1 g, 6.9 mmol), nitronium tetrafluoroborate (1.37 g, 10.35 mmol) (from Aldrich Chemical Company Ltd.), and 30 mL of acetic acid were added. The mixture was stirred at room temperature for 6 h and then poured into 100 mL of water. The resulting solution was extracted with ethyl acetate. The combined organic layer was washed with water and sodium bicarbonate solution and then dried over anhydrous magnesium sulfate. Magnesium sulfate was filtered off. The filtrate was chromatographed on a flash silica gel column by elution with ethyl acetate and hexane (v/v = 2:1). The first fraction was collected to give, in 15–16% conversion, 200 mg of compound 4 as a yellow solid; mp 182–184°C; IR (KBr, cm$^{-1}$): 3400(OH), 2230(C-N), 1590, 1540(NO$_2$), 1450, 1430(NO$_2$), 1360, 1240, 840; $^1$H NMR (DMSO-$d_6$) δ: 8.64 (s, 1H, H-C6), 7.62 (s, 1H, H-C3), 4.3 (br, s 1H, OH); MS m/z: 189 (M+, 100). Anal. calcd. for C$_9$H$_5$N$_2$O$_4$: C 50.81, H 1.60, N 22.22; found: C 50.84, H 1.28, N 21.98. Continuous elution with the same eluant gave 500 mg of the unreacted starting material 1. Further elution with ethyl acetate gave, in 13–14% conversion, 180 mg of compound 5, also as a yellow solid; mp >320°C; IR (KBr, cm$^{-1}$): 3400(OH), 2230(C-N), 1590, 1530(NO$_2$), 1475, 1380, 1340(NO$_2$), 1270, 840, 690; $^1$H NMR (DMSO-$d_6$) δ: 7.75 (d, J = 9 Hz, 1H, H-C6), 7.04 (d, J = 9 Hz, 1H, H-C5); MS m/z: 189 (M+, 100). Exact Mass calcd. for C$_9$H$_5$N$_2$O$_4$: 189.0174; found: 189.0180.

3,5-Dibromo-4-hydroxyphthalonitrile (6), 4-bromo-5-hydroxyphthalonitrile (7), and 3-bromo-4-hydroxyphthalonitrile (8)
A solution of 10 g (35.2 mmol) of N,N-dibromoisocyanuric
acid (NBI) (16) in 100 mL of concentrated H₂SO₄ was added in one portion to a solution of 7.8 g (54.2 mmol) of 4-hydroxyphthalonitrile (1) (12) in 100 mL of conc. H₂SO₄ at room temperature. The mixture was stirred for 10 min and then poured onto 800 g of ice. The resulting precipitate was filtered and the filtrate extracted three times with ethyl acetate. The extract was washed with water, a 2% solution of NaHCO₃, water, and dried over anhydrous MgSO₄. Evaporation of the solvent gave a mixture of products. Flash chromatography on silica gel and elution with ethyl acetate gave in the early fractions, in 12% yield, 2.0 g of 3,5-dibromo-4-hydroxyphthalonitrile (6) as a yellow-white solid, mp 269–271°C, IR (KBr, cm⁻¹): 3280 (OH), 2214 (CN); ¹H NMR (DMSO-d₆) δ: 11.16 (s, 1H, O-H), 8.38 (s, 1H, H-C6); MS m/z: 302 (M⁺, 100). Anal. calcld. for C₃H₅Br₂N₂O: C 31.83, H 0.67, N 9.28; found: C 31.82, H 0.65, N 9.00.

Further elution with ethyl acetate and evaporation of the solvent gave 2.1 g of a mixture of monobromo compounds. The original precipitate was extracted four times with ethyl acetate (leaving a residue of isocyanuric acid) and the extract dried, filtered, and evaporated as above to give an additional 6.6 g for an overall yield of 72% of an inseparable mixture of 4-bromo-5-hydroxyphthalonitrile (7) and 3-bromo-4-hydroxyphthalonitrile (8); ¹H NMR (DMSO-d₆) δ: 11.16 (s, O-H), 8.39 (s, H-C6 (7)), 8.08 (s, H-C3 (7)), 7.81 (d, H-C6 (8)), 7.30 (d, H-C3 (8)).

4-Methoxy-5-nitrophthalonitrile (9)
To 30 mg of compound 4 (0.16 mmol) in 20 mL of anhydrous ether, diazomethane (300 mg) in 30 mL of anhydrous ether was added dropwise at room temperature during a 30 min period. The evaporation of the ether gave, in 92% yield, 30 mg of compound 9; mp 94–96°C; IR (KBr, cm⁻¹): 3060, 2940, 2220 (C≡N), 1900, 1600, 1550, 1520 (NO₂), 1390, 1350, 1190, 1100, 980, 750; ¹H NMR (CDCl₃) δ: 8.2 (s, 1H, H-C6), 7.5 (s, 1H, H-C3), 4.1 (s, 3H, CH₃); MS m/z: 203 (M⁺, 100). Anal. calcld. for C₃H₄NO₂: C 53.21, H 2.48, N 20.68; found: C 53.49, H 2.29, N 20.53.

4-Methoxy-3-nitrophthalonitrile (10)
To 30 mg of compound 5 (0.16 mmol) in 20 mL of anhydrous ether, diazomethane (300 mg) in 30 mL of anhydrous ether was added dropwise at room temperature during a 30 min period. The solution was continuously stirred for 30 min. The evaporation of the ether gave, in 89% yield, 29 mg of compound 10; mp 110–112°C; IR (KBr, cm⁻¹): 3090, 2980, 2240 (C≡N), 1920, 1600, 1540 (NO₂), 1480 1360, 1280, 1060, 850, 780; ¹H NMR (CDCl₃) δ: 7.91 (d, J = 8.9 Hz, 1H, H-C6), 7.41 (d, J = 8.9 Hz, 1H, H-C3), 4.07 (s, 3H, CH₃); MS m/z: 203 (M⁺, 100). Anal. calcld. for C₃H₄NO₂: C 53.21, H 2.48, N 20.68; found: C 53.30, H 2.30, N 20.73.

4-Bromo-5-butoxyphthalonitrile (11) and 3-bromo-4-butoxyphthalonitrile (12)
To 50 mL of N,N-dimethylformamide (DMF) were added 4.0 g (18 mmol) of the mixture of 7 and 8, 4.7 g of K₂CO₃, and 4.5 g of 1-bromobutane. The mixture was stirred at 90°C for 2 h and then poured into 200 mL of water. The mixture was extracted twice with benzene and the extract washed twice with water and dried over anhydrous MgSO₄. The solvent was evaporated to give 7.6 g of a solid mixture. The mixture was separated by flash chromatography on silica gel using benzene–hexane (1:1) as eluant to give, in the first fractions, in 34% yield, 4-bromo-5-butoxyphthalonitrile (11); mp 117–119°C; IR (KBr, cm⁻¹): 2230 (CN); ¹H NMR (CDCl₃) δ: 7.93 (s, 1H, H-C6), 7.18 (s, 1H, H-C3), 4.13 (t, J = 4.2 Hz, 2H, OCH₂), 1.88 (m, 2H, OCH₂CH₃), 1.56 (m, 2H, CH₂CH₃), 1.01 (t, J = 4.9 Hz, 3H, CH₃); MS m/z: 278 (M⁺, 31). Anal. calcld. for C₁₃H₁₂BrN₂O: C 51.64, H 3.97, N 10.04; found: C 52.04, H 4.03, N 10.02.

Further elution gave 3-bromo-4-butoxyphthalonitrile (12) in 30% yield; mp 116–117°C; IR (KBr, cm⁻¹): 2235 (CN); ¹H NMR (CDCl₃) δ: 7.79 (d, J = 5.8 Hz, 1H, H-C6), 7.11 (d, J = 5.8 Hz, H-C3), 4.14 (t, J = 4.2 Hz, 2H, CH₂), 1.87 (m, 2H, OCH₂CH₃), 1.55 (m, J = 3.7 Hz, 2H, CH₂CH₃), 1.00 (t, J = 4.9 Hz, 3H, CH₃); MS m/z: 278 (M⁺, 76). Anal. calcld. for C₁₃H₁₂BrN₂O: C 51.64, H 3.97, N 10.04; found: C 51.76, H 3.86, N 9.95.

3-Aminophthalonitrile (14)
Nitrophthalonitrile (13) (21) was prepared using the procedure of Campagna et al. (12, 13) in 95% yield. The selective reduction of 13 was facilitated using a poisoned catalyst (22, 23). A mixture of 2.5 g of 5% palladium on barium sulfate and 5 mg of thiourea in 2.5 mL of methanol was shaken for 1 h. The solvent was evaporated and the brown residue homogenized. A suspension of 4.5 g (26 mmol) of 13 in 100 mL of dry dioxane–ethanol (3:1) containing 750 mg of the poisoned catalyst was hydrogenated at 30 psi (1 psi = 6.9 kPa) in a Parr hydrogenation bottle for 1 h at room temperature. The yellow solution was concentrated and purified by flash chromatography using tolune–acetanilide (5:1) as eluant to give 3.1 g (83% yield) of 14 as a yellow powdery solid, mp 210–212°C (lit. (31) mp 195–198°C).

3-Iodophthalonitrile (15)
Compound 14 (3.1 g, 21.7 mmol) was mixed with concentrated hydrochloric acid (62 mL) and ice (155 g), and sodium nitrite (2.35 g, 34.1 mmol) in water (20 mL) was added in one portion. After 1.5 h at 5°C, the solution was filtered. The diazonium salt solution was added dropwise to a stirred cool solution of potassium iodide in 30 mL of water. The resulting dark brown mixture was stirred for 0.5 h. This mixture was added to benzene and the solution was washed with cold water, cold 5% NaHCO₃, cold water, cold saturated Na₂S₂O₃, and again with cold water. The benzene solution was dried over anhydrous magnesium sulfate, filtered, and concentrated to a small volume. Chromatography on 200 g of normal grade silica gel and elution with benzene gave, in 62% yield, 3.3 g of pure 15 as white crystals, mp 167–169°C; IR (KBr, cm⁻¹): 3090, 2240 (CN), 1580, 1550, 1450, 1430, 1210, 1130, 810, 730; ¹H NMR (CDCl₃) δ: 8.16 (d, J = 8 Hz, 1H, ArH-6), 7.78 (d, J = 8 Hz, 1H, ArH-4), 7.40 (t, J = 8 Hz, 1H, ArH-5); MS m/z: 254 (M⁺), 202, 127, 100. Anal. calcld. for C₁₃H₈I₂N₂: C 37.82, H 1.19, N 0.13, 0.14, 0.15; found: C 38.36, H 1.10, N 0.12, 0.14, 0.15.
stream of argon for 5 min. The reaction flask was placed in an oil bath at 100–120°C and stirred under argon at this temperature until TLC analysis indicated that 15 was consumed (10 h). The reaction mixture was allowed to cool to room temperature and kept under argon overnight. The precipitate was filtered off and washed with toluene and diethyl ether to give, in 59% yield, 45 mg of compound 17 as an off-white solid; mp >330°C; IR (KBr, cm⁻¹): 3080, 2230 (C≡N), 1580, 1470, 1440, 1270, 1200, 1160, 801, 740. MS m/z: 280 (M⁺, 100). Anal. calcd. for C₇H₇N₄: C 77.14, H 2.86, N 20.00; found: C 77.24, H 2.39, N 20.27.

1,2-Bis-(2,3-dicyanophenyl)ethane (18)

By a procedure previously described (7, 8), 3.0 g (11.8 mmol) of 15, 80 mL of dry, freshly distilled diethylylamine, and 25 mg (0.133 mmol) of bis(triphenylphosphine) palladium dichloride was placed into a 250 mL two-necked flask, equipped with a magnetic stirrer, a condenser, and a gas inlet tube. The flask was flushed with argon and a moderate stream of dry acetonitrile was passed through the solution for 9 h at room temperature. A pale pink precipitate was observed. This mixture was evaporated and the remaining residue was washed with water, methanol, and diethyl ether. The crude product was extracted with methanol in a Soxhlet extractor for 12 h until the extract was almost clear. This process removed brown impurities. The pale pink compound was dried to give, in 88% yield, 1.44 g of 18, mp >300°C. This product is sufficiently pure that it can be used directly without further purification. Two recrystallizations of a small sample of 18 from acetonitrile gave white crystals of pure 18, mp >300°C; IR (KBr, cm⁻¹): 3090, 2240 (CN), 1590, 1480, 1450, 1340, 1290, 810, 710; ¹H NMR (DMSO-d₆, 300 MHz) δ: 8.25 (d, J = 8 Hz, 2H, ArH-6), 8.16 (d, J = 8 Hz, 2H, ArH-4), 8.01 (t, J = 8 Hz, 2H, ArH-5); MS m/z: 278 (M⁺), 251, 224, 200, 176, 139. Anal. calcd. for C₁₈H₁₂N₄: C 77.69, H 2.17, N 20.13; found: C 77.42, H 2.08, N 20.78.

1,2-Bis-(2,3-dicyanophenyl)ethane (19)

A suspension of 0.200 g (0.72 mmol) of 18 in 150 mL of acetonitrile containing 50 mg of 10% palladium on charcoal was hydrogenated at 65 psi in a Parr hydrogenation bottle for 4 h at room temperature. The clear solution was filtered from the catalyst and concentrated. The compound was purified by flash chromatography using acetonitrile as eluant to give 0.190 g (94% yield) of 19 as yellow needles, mp 246–248°C; IR (KBr, cm⁻¹): 3090–2920, 2230 (CN), 1590, 1480, 820, 750; ¹H NMR (DMSO-d₆, 300 MHz) δ: 8.01 (d, J = 8 Hz, 2H, ArH-6), 7.81 (t, J = 8 Hz, 2H, ArH-5), 7.72 (d, J = 8 Hz, 2H, ArH-4), 3.28 (s, 4H, CH₂CH₂O); MS m/z: 282 (M⁺), 255, 226, 201, 141. Anal. calcd. for C₁₈H₁₆N₄: C 76.58, H 3.57, N 19.84; found: C 76.32, H 3.69, N 19.99.

2-Bromomethyl-3-dibromomethylnitrobenzene (21)

To a 1000 mL one-necked round-bottomed flask, charged with 500 mL of carbon tetrachloride, 3-nitro-o-xylene (20) (10 g, 66 mmol) (from Aldrich Chemical Company Ltd), N-bromosuccinimide (70.88 g, 396 mmol), and 200 mg of benzoyl peroxide were added. The mixture was irradiated using a 270 W sun lamp for 12 h or until TLC analysis indicated that the 3-nitro-o-xylene (20) was consumed. A precipitate was formed and the hot solution was filtered. The filtrate was concentrated, preabsorbed on a small amount of flash silica gel, and then loaded on a 5 cm diameter column containing flash silica gel and eluted with cyclohexane. The second fraction was collected to give 17 g of compound 21 in 83% yield; mp 67–68°C; IR (KBr cm⁻¹): 3080, 3020, 1520 (NO₂), 1440, 1380 (NO₂), 1255, 1230, 1140, 930, 850, 820, 780, 575, 640; ¹H NMR (CDCl₃) δ: 8.28 (d, J = 7.3 Hz, 1H, H-C₃), 7.86 (dd, J = 7.3, 1.5 Hz, 1H, H-C₄), 7.59 (t, J = 8 Hz, 1H, H-C₅), 7.12 (brs, 1H, CH₃Br), 4.72 (s, 2H, CH₂Br); ¹³C NMR (CDCl₃) δ: 143.0, 135.0, 131.2, 130.2, 126.5, 125.9, 34.4, 21.4; MS m/z: 306 (M⁺ → 79), 308, 310, 384 (M⁺ → 1), 386, 388, 390. Exact Mass calcd. for C₃H₇Br₂NO₂: 383.7871 (M⁺ → H); found 383.7873.

S-Aminonaphthalene-2,3-dicarbonitrile (24)

Nitronaphthalene-2,3-dicarbonitrile (23), prepared from 19 and furanornitrite (22) by the procedure of Kovshev et al. (9a), gave, upon hydrogenation as for the preparation of 13 above, the known 24, mp 256–258°C (lit. (26) mp 257–258°C).

5-Iodonaphthalene-2,3-dicarbonitrile (25)

A solution of concentrated H₂SO₄ (12 mL) and ice (50 g) was cooled to 0°C on a salt–ice bath. Compound 24 (300 mg, 1.6 mmol) was added to this solution followed by an aqueous solution of sodium nitrite (176.5 mg, 2.56 mmol). The resulting solution was stirred for 1 h at 0°C and then added dropwise to 20 mL of an aqueous solution of sodium iodide (5 g), which was vigorously stirred and kept below 3°C. After 0.5 h at 3°C, the dark brown solution was allowed to slowly warm to room temperature. Benzene (50 mL) was added to the dark brown solution. After stirring for 10 min, the resulting mixture was filtered. The organic layer was separated and washed with cold water, 10% NaHCO₃, cold water, a cold saturated solution of Na₂SO₃, again with cold water, and then dried over anhydrous magnesium sulfate for 2 h. The magnesium sulfate was filtered off. The filtrate was concentrated to a small volume and chromatographed on a column containing regular grade silica gel using toluene as the eluant to give, in 46% yield, 270 mg of compound 25 as a yellow solid; mp 243°C; IR (KBr, cm⁻¹): 3080, 2240, (C≡N), 1540, 1430, 918, 900; ¹H NMR (DMSO-d₆, 300 MHz) δ: 8.88 (s, 1H, H-Cl), 8.61 (s, 1H, H-C₄), 8.48 (d, J = 8 Hz, 1H, H-C₆), 8.19 (d, J = 8 Hz, 1H, H-C₈), 7.62 (t, J = 8 Hz, 1H, H-C₇); ¹³C NMR (DMSO-d₆) δ: 142.3, 139.4, 137.5, 134.0, 133.0, 132.0, 129.8, 116.0, 115.9, 110.8, 109.9, 100.3; MS m/z: 304 (M⁺, 100). Anal. calcd. for C₁₃H₁₀N₂: C 47.40, H 1.66, N 9.21; found: C 47.76, H 1.55, N 8.94.

trans-1,2-Bis(6,7-dicyanophenyl)ethene (26)

To a 50 mL round-bottom flask equipped with a magnetic stirrer, 5-iodonaphthalene-2,3-dicarbonitrile (25) (300 mg, 0.96 mmol), compound 16 (290 mg, 0.48 mmol), toluene (25.0 mL), and tetrakis(triphenylphosphine) palladium(0) (33.5 mg, 0.029 mmol) were added. The resulting mixture was degazetated with a stream of argon for 5 min. The reaction flask was placed in an oil bath at 100–120°C and stirred under argon at this temperature until TLC analysis indicated that 25 was consumed (about 10 h). The reaction mixture was allowed to cool to room temperature and remained under argon overnight. The precipitate was filtered and washed with toluene and diethyl ether to give, in 80% yield, 150 mg of compound
trans-1,2-Bis(3,4-dicyanophenylethene) (29)

To a 50 mL round-bottomed flask equipped with a magnetic stirrer, 4-iodophthalonitrile (28) (517 mg, 1.96 mmol), compound 16 (594 mg, 0.98 mmol), toluene (5 mL, freshly distilled over sodium), and tetrakis(triphenylphosphine)palladium(0) (21.7 mg, 0.018 mmol) (from Aldrich Chemical Company Ltd) were added. The resulting mixture was deoxygenated with a stream of argon for 5 min. The reaction flask was placed in an oil bath at 100–120°C and stirred under argon at this temperature until TLC analysis indicated that 28 was consumed (about 10 h). The reaction mixture was allowed to cool to room temperature and remained under argon overnight. The precipitate was filtered off and washed with toluene and diethyl ether to give, in 98% yield, 279 mg of compound 29; mp >330°C; IR (KBr, cm⁻¹): 3050, 2220 (C≡N), 1590, 1490, 1415, 1325, 960, 910, 840, 725; ¹H NMR (DMSO-d₆) δ: 8.84 (s, 2H, H-C₂), 8.17 (d, J = 8.2, H-C₅), 8.07 (br, d, J = 8.2, 2H, H-C₆), 7.71 (s, 2H, H=CC≡N); MS m/z: 280 (M⁺, 100). Anal. calcd. for C₁₉H₁₀N₄: C 77.13, H 2.88, N 19.95; found: C 76.96, H 2.57, N 19.64.

2,3,6,7-Tetracyanophanthenes (31) and 2,3,5,6-tetracyanophanthenes (32)

To 90 mL of dioxane in a Pyrex tube (40 x 5 cm), trans-29 (40 mg, 0.14 mmol) or cis-30 (26) (40 mg, 0.14 mmol) and iodine (25 mg, 0.19 mmol) were added. The suspension was sonicated until all particulates were dissolved. The tube was placed in a Rayonet photochemical reactor and irradiated for 9 h (the wavelength emitted by the lamps used was in the range of 257–350 nm). In the irradiation of 29 a trace amount of precipitate was removed by filtration. The solution was washed with a saturated solution of sodium bisulfite and then with ethyl acetate. The organic layer was separated and dried over anhydrous MgSO₄. After filtering the MgSO₄, the solution was concentrated. The concentrated solution was preadsorbed on a small amount of flash silica gel, then loaded on a column containing TLC grade silica gel G and eluted slowly over a 12 day period with hexane – ethyl acetate (3:1). The first fraction gave, in 31 and 40% yield from 29 and 30, respectively, 12.2 and 15.9 mg of compound 31; mp >330°C; IR (KBr, cm⁻¹): 3065, 3040, 2240 (C≡N), 1595, 1245, 920; ¹H NMR (DMSO-d₆) δ: 8.84 (s, 2H, H-C₁, H-C₈), 8.99 (s, 2H, H-C₄, H-C₅), 8.33 (s, 2H, H-C₉, H-C₁₀); ¹³C NMR (DMSO-d₆) δ: 136.1, 134.2, 132.1, 130.6, 130.3, 116.1, 115.9, 112.6, 111.7; MS m/z: 278 (M⁺, 100). Anal. calcd. for C₁₆H₁₂N₄: C 77.69, H 2.17, N 20.13; found: C 77.33, H 2.34, N 19.88.

Further elution with the same solvents gave, in 28 and 36% yields from 29 and 30, respectively, 11.0 and 14.2 mg of compound 32; mp >330°C; IR (KBr, cm⁻¹): 3395, 2220 (C≡N), 1585, 925, 870; ¹H NMR (DMSO-d₆) δ: 10.07 (s, 1H, H-C₄), 9.03 (s, 1H, H-C₁), 8.67 (d, J = 8.4, 1H, H-C₈), 8.47 (d, J = 8.4, 1H, H-C₇), 8.39 (d, J = 8.9, 1H, H-C₉), 8.31 (d, J = 8.9, 1H, H-C₁₀); ¹³C NMR (DMSO-d₆) δ: 136.4, 125.9, 135.5, 134.8, 131.4, 131.1, 130.5, 128.9, 127.4, 118.5, 117.8, 116.4, 116.2, 115.6, 112.0, 111.1; MS m/z: 278 (M⁺, 100). Anal. calcd. for C₁₉H₁₀N₄: C 77.69, H 2.17, N 20.13; found: C 77.20, H 2.33, N 19.91.

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References


