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-hydroxyphthalonitrile gave 4-hydroxy-3-nitrophthalonitrile and 4-hydroxy-5-nitrophthalonitrile, while bromination yielded 3-bromo-4-hydroxyphthalonitrile, 4-bromo-5-hydroxyphthalonitrile, and 3,5-dibromo-4-hydroxyphthalonitrile. Iodination gave 4-hydroxy-5-iodophthalonitrile and 4-hydroxy-3,5-diidophthalonitrile. 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-tetracyanophenanthrenes separable by chromatography.

Key words: phthalonitriles, naphthalenedicarbonitriles, phenanthrenetetracarbonitriles, electrophilic substitution.

Résumé : La nitration électrophile aromatique du 4-hydroxyphtalonitrile, dans des conditions douces, conduit au 4-hydroxy-3-nitrophtalonitrile et au 4-hydroxy-5-nitrophtalonitrile alors que sa bromation fournit du 3-bromo-4-hydroxyphtalonitrile, du 4-bromo-5-hydroxyphtalonitrile, et du 3,5-dibromo-4-hydroxyphtalonitrile. L'iodation fournit du 4-hydroxy-5-iodophtalonitrile et du 4-hydroxy-3,5-diiodophtalonitrile. Le couplage des 4-iodophtalonitrile, 3-iodophtalonitrile et 5-iodo-2,3-dicyanonaphtalène 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-dicyanonaphtyl)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-tétracyanophénanthrènes que l'on peut séparer par chromatographie.

Mots clés : phtalonitriles, naphtalènedicarbonitriles, phénanthrènetétracarbonitriles, 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 cyanation 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.

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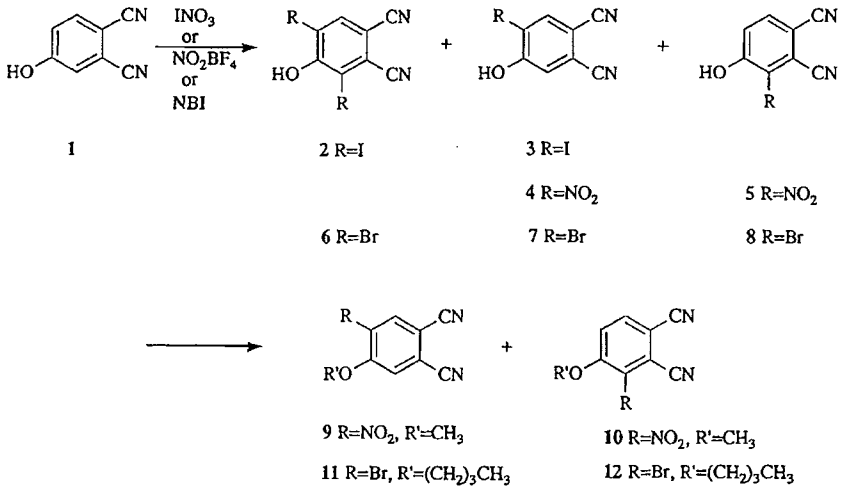
Iodination, nitration, and bromination of 4-hydroxyphthalonitrile (1)

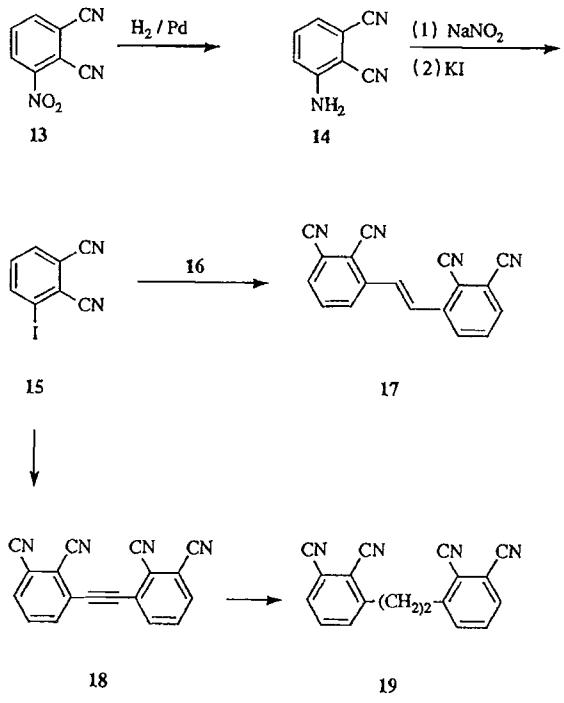
A recent paper by Gaude et al. (14) described the direct iodination of phenols by iodine nitrate and we thought that this procedure could be successful in the direct iodination of 4-hydroxyphthalonitrile (**1**)(15) as the two nitrile groups may not sufficiently deactivate phenol **1** towards electrophilic 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-diiodophthalonitrile (**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

Scheme 1



Scheme 2



led us to consider direct nitration of **1**, using the mild nitrating reagent nitronium tetrafluoroborate (16). Nitration of **1** with nitronium tetrafluoroborate in acetic acid at room temperature, followed by flash chromatography (17) and vacuum liquid chromatography (18) of the reaction mixture, gave 4-hydroxy-5-nitrophthalonitrile (**4**) and 4-hydroxy-3-nitrophthalonitrile (**5**) in 15 and 13% yield, respectively (Scheme 1).

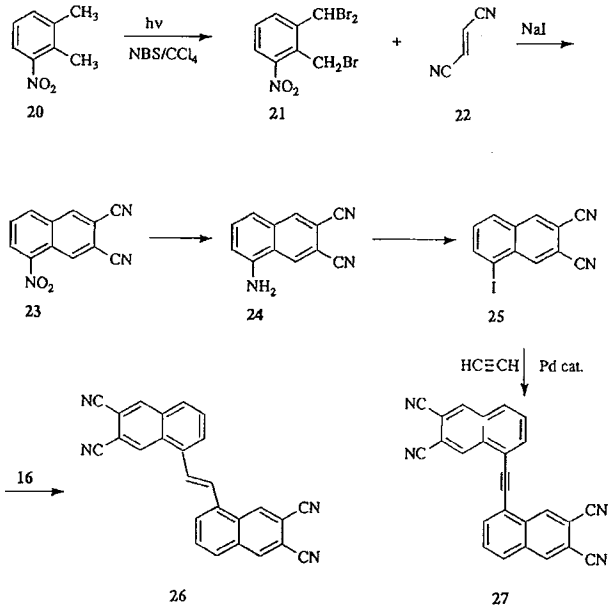
Since the yields of **4** and **5** were still unsatisfactory, we decided to try a rarely used brominating agent, *N,N*-dibromoisocyanuric (NBI) acid (19, 20) known to brominate aromatic compounds containing both activating and deactivating substituents. Although sulfuric acid is used in this procedure, 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-hydroxyphthalonitrile (**6**) and a mixture of monobromo-4-hydroxyphthalonitriles consisting of 4-bromo-5-hydroxyphthalonitrile (**7**) and 3-bromo-4-hydroxyphthalonitrile (**8**) in 72% yield that was inseparable by flash chromatography. Chromatography of the product mixtures of **4** and **5** and of **7** and **8** proved to be quite tedious. Hence the mixture of **4** and **5** was treated with diazomethane to give the less polar 4-methoxy-5-nitrophthalonitrile (**9**) and 4-methoxy-3-nitrophthalonitrile (**10**), while the mixture of **7** and **8** was alkylated using K_2CO_3 and 1-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).

Bisdicyanoarylethenes from dicyanoiodoarenes

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)ethyne (**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)ethane (**19**) (Scheme 2).

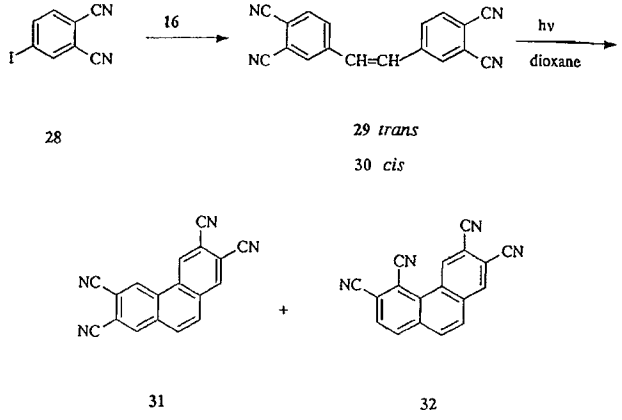
Bromination (9) of 2,3-dimethyl–1-nitrobenzene (**20**) gave 2-bromomethyl-3-dibromomethyl–1-nitrobenzene (**21**), which on treatment (9) with sodium iodide in *N,N*-dimethylformamide and fumaronitrile (**22**) yielded the known 5-iodo-2,3-dicyanonaphthalene (**23**), prepared by a different route (26). Reduction of **23** (26), gave 5-amino-2,3-dicyanonaphthalene (**24**) (26), which upon diazotization and treatment with potassium iodide gave the unknown 5-iodonaphthalene-2,3-dicarbonitrile (**25**). Coupling of **25** with **16** gave *trans*-1,2-bis(6,7-dicyanonaphthyl)ethene (**26**) (Scheme 3). Both

Scheme 3



20 21 22 23 24 25 26 27

Scheme 4



28 29 *trans* 30 *cis* 31 32

arylethenes **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)ethene (**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 $CHBr_2$ group to give a doublet of doublets (see Experimental), and hence the $CHBr_2$ group is at the 3 position.

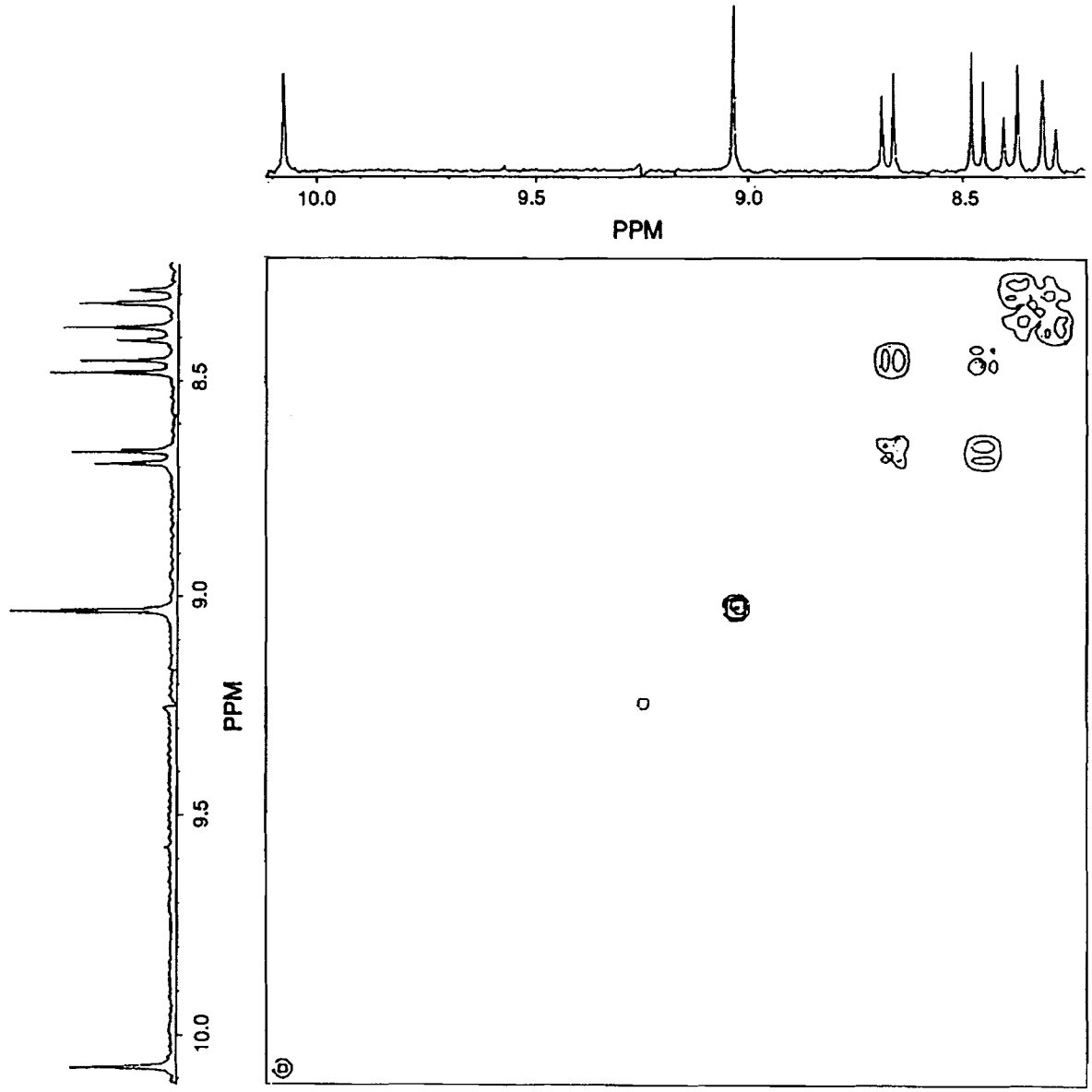
A NOESY spectrum of compound **25** exhibited long-range coupling between the singlet at 8.88 ppm (H-C1) and the doublet at 8.20 ppm (H-C8). Thus, the other singlet at 8.61 ppm is H-C4, the doublet at 8.49 is H-C6, and the triplet at 7.62 is H-C7. The HH-COSY and NOESY spectra of **32** (Figs. 1 and 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, bisphthalonitriles, 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), hextets (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 Kofler 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

Fig. 1. The ^1H–^1H COSY NMR spectrum of 2,3,5,6-tetracyanophenanthrene (**32**) in DMSO-d_6.

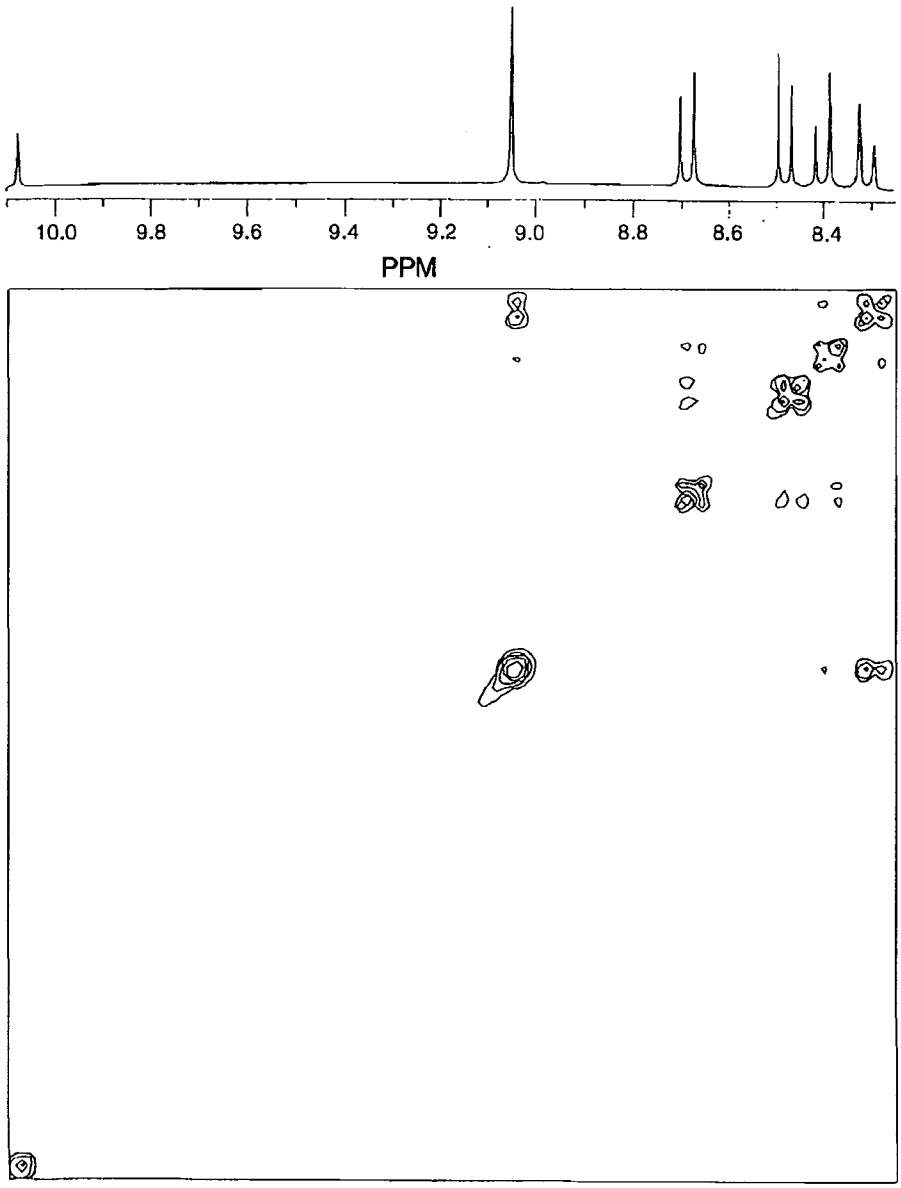


solvents were freshly distilled before use. Microanalysis were performed by Guelph Chemical Laboratory Ltd., Guelph, Ontario. Thin-layer chromatography (TLC) was performed using silica gel G as the absorbent.

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, 1280, 1170, 1120, 900; ^1H NMR (DMSO-d_6) δ: 9.50 (s, 1H, O*H*), 8.52 (s, 1H, *H*-C6 or *H*-C3), 8.48 (s, 1H, *H*-C3 or *H*-C6); MS *m/z*: 270 (M^+, 100). Exact Mass calcd. for $C_8H_3N_2IO$: 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-d_6) δ: 8.43 (s, 1H, *H*-C6), 4.3 (br, s, 1H, O*H*). Exact Mass calcd. for $C_8H_2N_2I_2O$: 395.8255; found: 395.8255.

Fig. 2. The ^1H–^1H NOESY NMR spectrum of 2,3,5,6-tetracyanophenanthrene (**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}): 3280 (OH), 2250 (C≡N), 1630, 1565 (NO_2), 1320 (NO_2), 1280, 1120, 740; ^1H NMR (DMSO-d_6) δ: 8.64 (s, 1H, *H*-C6), 7.62 (s, 1H, *H*-C3), 4.3 (br, s 1H, O*H*); MS *m/z*: 189 (M+, 100). Anal. calcd. for $C_8H_3N_3O_3$: 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; ^1H 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 $C_8H_3N_3O_3$: 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 H_2SO_4 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. H_2SO_4 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 $NaHCO_3$, water, and dried over anhydrous $MgSO_2$. 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-d_6) δ: 11.16 (s, 1H, O-H), 8.38 (s, 1H, *H*-C6); MS *m/z*: 302 (M+, 100). Anal. calcd. for $C_8H_2Br_2N_2O$: 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-d_6) 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 (NO_2), 1390, 1350, 1190, 1100, 980, 750; ^1H NMR ($CDCl_3$) δ: 8.2 (s, 1H, *H*-C6), 7.5 (s, 1H, *H*-C3), 4.1 (s, 3H, CH_3); MS *m/z*: 203 (M^+, 100). Anal. calcd. for $C_9H_5N_3O_3$: 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 (NO_2), 1480 1360, 1280, 1060, 850, 780; ^1H NMR ($CDCl_3$) δ: 7.91 (d, J = 8.9 Hz, 1H, *H*-C6), 7.41 (d, J = 8.9 Hz, 1H, *H*-C5), 4.07 (s, 3H, CH_3); MS *m/z*: (M^+, 100). Anal. calcd. for $C_9H_5N_3O_3$: 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 K_2CO_3, 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 $MgSO_4$. 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 ($CDCl_3$) δ: 7.93 (s, 1H, *H*-C6), 7.18 (s, 1H, *H*-C3), 4.13 (t, J = 4.2 Hz, 2H, OC*H*2), 1.88 (m, 2H, OCH_2CH_2), 1.56 (m, 2H, CH_3CH_2), 1.01 (t, J = 4.9 Hz, 3H, CH_3); MS *m/z*: 278 (M^+, 31). Anal. calcd. for $C_{12}H_{11}BrN2O$: 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 ($CDCl_3$) 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, CH_2), 1.87 (m, 2H, OCH_2CH_2), 1.55 (m, J = 3.7 Hz, 2H, CH_3CH_2), 1.00 (t, J = 4.9 Hz, 3H, CH_3); MS *m/z*: 278 (M^+, 76). Anal. calcd. for $C_{12}H_{11}BrN_2O$: 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 toluene–acetonitrile (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% $NaHCO_3$, cold water, cold saturated $Na_2S_2O_3$, 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 ($CDCl_3$) δ: 8.16 (d, J = 8 Hz, 1H, Ar*H*-6), 7.78 (d, J = 8 Hz, 1H, Ar*H*-4), 7.40 (t, J = 8 Hz, 1H, Ar*H*-5); MS *m/z*: 254 (M^+), 202, 127, 100. Anal. calcd. for $C_8H_3N_2I$: C 37.82, H 1.19, N. 11.03, I 49.95; found: C-38.36, H 1.10, N 11.20, I 49.81.

trans-*1,2-Bis(2,3-dicyanophenyl)ethene (17)*

To a 50 mL round-bottomed flask equipped with a magnetic stirrer were added 3-iodophthalonitrile (**15**) (132 mg, 0.52 mmol), compound **16** (157.6 mg, 0.26 mmol), toluene (25.0 mL), and tetrakis(triphenylphosphine) palladium(0) (18.6 mg, 0.016 mmol). 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 **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 $C_{18}H_8N_4$: 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)ethyne (**18**)*

By a procedure previously described (7, 8), 3.0 g (11.8 mmol) of **15**, 80 mL of dry, freshly distilled diethylamine, 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 acetylene 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, 1190, 810, 710; ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 8.25 (d, J = 8 Hz, 2H, Ar*H*-6), 8.16 (d, J = 8 Hz, 2H, Ar*H*-4), 8.01 (t, J = 8 Hz, 2H, Ar*H*-50; MS *m/z*: 278(M^+), 251, 224, 200, 176, 139. Anal. calcd. for $C_{18}H_6N_4$: 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; ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 8.01 (d, J = 8 Hz, 2H, Ar*H*-6), 7.81 (t, J = 8 Hz, 2H, Ar*H*-5), 7.72 (d, J = 8 Hz, 2H, Ar*H*-4), 3.28 (s, 4H, CH_2CH_2O; MS *m/z*: 282(M^+), 255, 226, 201, 141. Anal. calcd. for $C_{18}H_{10}N_4$: 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, 745, 680, 640; ^{1}H NMR ($CDCl_3$) δ: 8.28 (d, J = 7.3 Hz, 1H, *H*-C_6), 7.86 (dd, J = 7.3, 1.0 Hz, 1H, *H*-C4), 7.59 (t, J = 8 Hz, 1H, *H*-C5), 7.12 (brs, 1H, C*H*Br_2), 4.72 (s, 2H, CH_2Br); ^{13}C NMR ($CDCl_3$) 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 $C_8H_6Br_3NO_2$: 383.7871 (M^+−H); found 383.7873.

*5-Aminonaphthalene-2,3-dicarbonitrile (**24**)*

Nitronaphthalene-2,3-dicarbonitrile (**23**), prepared from **19** and fumaronitrile (**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 H_2SO_4 (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% $NaHCO_3$, cold water, a cold saturated solution of $Na_2S_2O_3$, 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, 800; ^{1}H NMR (DMSO-d_6) 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): ^{13}C NMR (DMSO)-d_6) 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 $C_{12}H_8N_2$: 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-dicyanonaphthyl)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 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 **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

26 as a green-yellow solid; mp >330°C; IR (KBr, cm^{-1}): 3050, 2220 (C≡N), 1450, 1370, 1360, 1340, 960, 901, 801, 750. Exact Mass calcd. for $C_{26}H_{12}N_4$: 380.1061; found: 380.1064.

1,2-Bis(6,7-dicyanonaphthyl)ethyne (27)

Compound **25** (265 mg, 0.87 mmol), 25 mL of dry, freshly distilled diethylamine, 25 mg of copper(I) iodide (0.133 mmol), and 20 mg of bis(triphenylphosphine)palladium dichloride (0.028 mmol) were added to a 100 mL two-necked round-bottomed flask, which was equipped with a magnetic stirrer, a condensor, and a gas inlet tube. The flask was first flushed with argon and then a moderate stream of dry acetylene was bubbled though the solution for 6 h at room temperature. A brown precipitate was produced. The precipitate was filtered off and extracted continuously with methanol in a Soxhlet apparatus for about 12 h, or until the extract was colourless. The precipitate in the thimble was dried in an oven at 100°C for 2 h, to give, in 54% yield, 178 mg of compound **27** as a brown solid; mp >330°C; IR (KBr, cm^{-1}): 3060, 2230 (C≡N), 1580, 1260, 1180, 900, 800, 750; MS *m/z*: 378 (M^+, 100). Exact Mass calcd. for $C_{26}H_{10}N_4$: 378.0905; found: 378.0917.

trans-*1,2-Bis(3,4-dicyanophenyl)ethene (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 (5.0 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; ^{1}H NMR (DMSO-d_6) δ:8:41 (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, *HC*=*CH*); MS *m/z*: 280 (M^+, 100). Anal. calcd. for $C_{18}H_8N_4$: C 77.13, H 2.88, N 19.95; found: C 76.96, H 2.57, N 19.64.

2,3,6,7-Tetracyanophenanthrene (31) and 2,3,5,6-tetracyanophenanthrene (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 $MgSO_4$. After filtering the $MgSO_4$, 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-d_6) δ: 9.86 (s, 2H, *H*-C1, *H*-C8), 8.99 (s, 2H, *H*-C4, *H*-C5), 8.33 (s, 2H, *H*-C9, *H*-C10); ^{13}C NMR (DMSO-d_6) 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 $C_{18}H_6N_4$: 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; ^{1}H NMR (DMSO-d_6) 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); ^{13}C NMR (DMSO-d_6) 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, 112.6, 112.0, 111.1; MS *m/z*: 278 (M^+, 100). Anal. calcd. for $C_{18}H_6N_4$: C 77.69, H 2.17, N 20.13; found: C 77.20, H 2.33, N 19.91.

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