Investigation of the Reaction of 2-Bromo-1,4-dimethoxynaphthalene and 9-Bromophenanthrene with Nitriles Under Aryne-Forming Conditions

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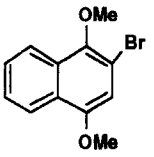
The reaction of 2-bromo-1,4-dimethoxynaphthalene (**1**) and 9-bromophenanthrene (**3**) with nitriles **2** under base-mediated, aryne-forming conditions gives product distributions which depend upon the nature of the bromoarene, nitrile, base, and the reaction medium. Thus, treatment of **1** with arylacetonitriles **2a–d** in the presence of LDA in THF or sodium amide in liquid ammonia supplies α-aryl-1,4-dimethoxy-2-naphthylacetonitriles **4a–d**, presumably by the aryne arylation mechanism. In contrast, the reaction of 9-bromophenanthrene (**3**) and arylacetonitriles **2b–e** with LDA in THF yields 10-arylmethyl-9-phenanthrenecarbonitriles **6b–e**, most likely by the tandem addition–rearrangement pathway. When **3** reacts with **2a–c** in the presence of sodium amide and liquid ammonia, α-aryl-9-phenanthrylacetonitriles **5a–c**, rather than the rearranged nitriles **6a–c**, are obtained. Both **1** and **3** react with alkylnitriles **2f–i** and LDA–THF, sodium amide–liquid ammonia, or Caubere's sodamide base to afford aryne arylated nitriles (**4f–i** and **5f–i**, respectively). An explanation in terms of the influence of reactants and solvent on the competition between the aryne arylation and tandem addition–rearrangement pathways is presented.

We observed previously that the position of the triple bond in the two isomeric naphthalynes influences the course of their reactions with α-metalated nitriles.[1] For example, α-lithio(aryl)acetonitriles react with 3-methoxy-1,2-naphthalyne to yield predominantly 1-arylmethyl-3-methoxy-2-naphthalenecarbonitriles, presumably by the tandem addition–rearrangement pathway.[2] In contrast, these α-lithio nitriles, when treated with 1,4-dimethyl-2,3-naphthalyne, supply α-aryl-1,4-dimethyl-2-naphthylacetonitriles, probably by the aryne mechanism.[3] Both isomeric naphthalynes, however, afford α-alkyl naphthylacetonitriles when they react with α-lithioalkanenitriles. To obtain more information on the influence of the position of the triple bond of arynes derived from polyarenes on nitrile product distributions, we have investigated the reaction of 2-bromo-1,4-dimethoxynaphthalene (**1**) with arylacetonitriles **2a–d**, and the reaction of 9-bromophenanthrene (**3**) with arylacetonitriles **2b–e** under aryne-forming conditions (LDA–THF and sodium amide–liquid ammonia), and report the results herein. The reaction of **1** and **3** with alkanenitriles **2f–i** and sodium amide in liquid ammonia was also studied. The resulting α-alkylnitriles (**4f–i** and **5f–i**, respectively) should serve as valuable precursors to potentially important biologically active materials since they can be oxidized to 1,4-naphthoquinones and their α-CHRCN side chains (R = H, Me, Et, Pr) can be hydrolyzed and reduced to $CHRCO_2H$ and $CHRCH_2NH_2$ groups, respectively.

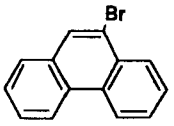
The results of the reaction of 2-bromo-1,4-dimethoxynaphthalene (**1**) and 9-bromophenanthrene (**3**) with various nitriles **2** are given in the Table. The data show that only the reaction of **3** with arylacetonitriles **2b–e** and LDA in THF (entries 26–29) afford rearranged nitriles, i.e. 10-arylmethyl-9-phenanthrenecarbonitriles **6b–e**. The yields of **6b–e** were generally good, ranging from 51 to 84%. When **3** and **2a–c** were treated with sodium amide in liquid ammonia, α-aryl-9-phenanthrylacetonitriles **5a–c** were obtained albeit in low yields (28–43%) (entries 15–17). Detracting from the yields of **5a–c** was the formation of fair amounts (10–30%) of 9-aminophenanthrene, resulting presumably from the amination of 9,10-phenanthryne by the ammonia solvent. Attempts to increase the yields of **5a–c** by decreasing the amount of ammonia were unsuccessful. In contrast, the reaction of **1** with arylacetonitriles **2a–d** with either LDA in THF or sodium amide in liquid ammonia supplied arylated products, α-aryl-1,4-dimethoxy-2-naphthylacetonitriles **4a–d**; the yields of **4a–d** were slightly higher in the sodium amide mediated reactions (44–49%, entries 5–8) than those from the LDA reactions (33–41%, entries 1–4). That no significant advantage was gained by using the LDA–THF in place of the sodium amide–ammonia system was somewhat unexpected since the use of sterically demanding bases such as LDA usually results in decreased yields of aryne aminated products and increased yields of aryne arylated products.[4] Although the yields of 9-*N*,*N*-diisopropylaminophenanthrene were indeed quite low (< 10%) in the aforementioned reactions, significant amounts (15–28%) of phenanthrene were also obtained, most likely from the reduction of **3** or 9,10-phenanthryne by LDA.[5]



1

RCH_2CN

2a, R = C_6H_5
2b, R = 4'-MeO-C_6H_4
2c, R = 3'-MeO-C_6H_4
2d, R = 3', 4'-di-MeO-C_6H_3
2e, R = 3', 4', 5'=tri-MeOC_6H_2
2f, R = H
2g, R = CH_3
2h, R = CH_3CH_2
2i, R = $CH_3CH_2CH_2$



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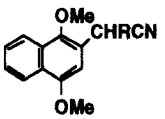
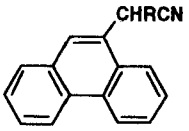
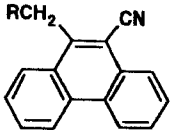


4a, R = C_6H_5
4b, R = 4'-MeO-C_6H_4
4c, R = 3'-MeO-C_6H_4
4d, R = 3',4'-di-MeO-C_6H_3
4g, R = CH_3
4h R = CH_3CH_2
4i, R = $CH_3CH_2CH_2$



5a, R = C_6H_5
5b, R = 4'-MeOC_6H_5
5c, R = 3'-MeOC_6H_5
5f, R = H
5g R = CH_3
5h, R = CH_3CH_2
5i R = $CH_3CH_2CH_2$



6b, R = 4'-MeO-C_6H_4
6c, R = 3'-MeO-C_6H_4
6d, R = 3',4'-di-MeO-C_6H_3
6e, R = 3',4',5-tri-MeO-C_6H_2

Table. Reaction of Halopolyarenes **1** or **3** with Nitriles **2** and LDA or $NaNH_2$

Entry	Halo-arene	Nitrile	Base	Product	Yield (%)
1	**1**	**2a**	LDA	**4a**	33
2	**1**	**2b**	LDA	**4b**	37
3	**1**	**2c**	LDA	**4c**	39
4	**1**	**2d**	LDA	**4d**	41
5	**1**	**2a**	$NaNH_2$[a]	**4a**	45
6	**1**	**2b**	$NaNH_2$	**4b**	49
7	**1**	**2c**	$NaNH_2$	**4c**	45
8	**1**	**2d**	$NaNH_2$	**4d**	44
9	**1**	**2f**	$NaNH_2$	**4f**	69[d]
10	**1**	**2f**	$NaNH_2$[b]	**4f**	56[e]
11	**1**	**2f**	$NaNH_2$[c]	**4f**	31[f]
12	**1**	**2g**	$NaNH_2$	**4g**	79
13	**1**	**2h**	$NaNH_2$	**4h**	68
14	**1**	**2i**	$NaNH_2$	**4i**	52
15	**3**	**2a**	$NaNH_2$	**5a**	28
16	**3**	**2b**	$NaNH_2$[a]	**5b**	43
17	**3**	**2c**	$NaNH_2$	**5c**	35
18	**3**	**2f**	$NaNH_2$[a]	**5f**	31[g]
19	**3**	**2g**	$NaNH_2$[a]	**5g**	27[h]
20	**3**	**2h**	$NaNH_2$	**5h**	27[i]
21	**3**	**2i**	$NaNH_2$	**5i**	26[j]
22	**3**	**2f**	LDA	**5f**	30
23	**3**	**2g**	LDA	**5f**	26
24	**3**	**2h**	LDA	**5h**	33
25	**3**	**2f**	$NaNH_2$[k]	**5f**	40[l]
26	**3**	**2b**	LDA	**6b**	64
27	**3**	**2c**	LDA	**6c**	69
28	**3**	**2d**	LDA	**6d**	84
29	**3**	**2e**	LDA	**6e**	51

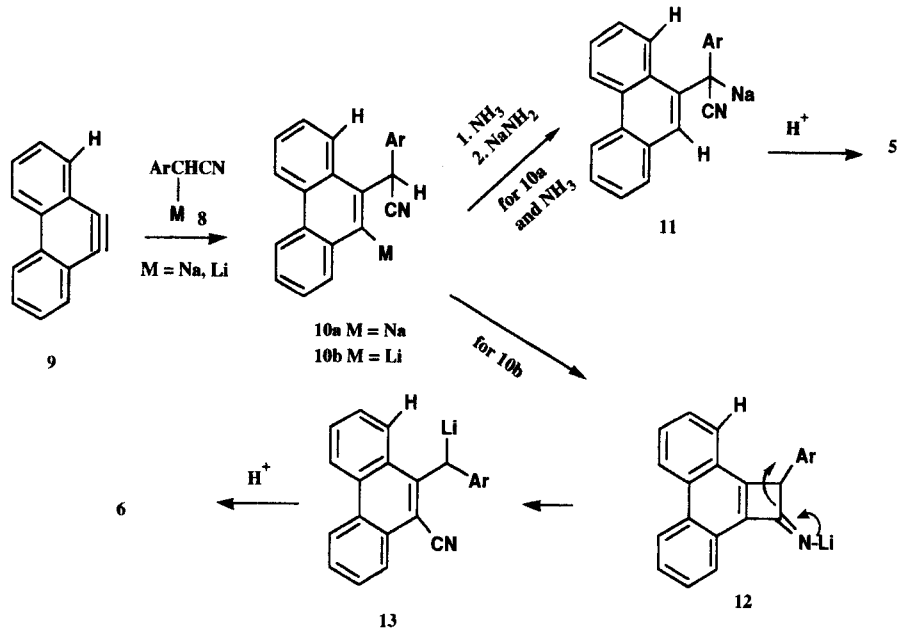
[a] Unless stated otherwise, the molar ratio of reactants used was 0.2 mol $NaNH_2$/100 mL NH_3.
[b] 0.5 mol $NaNH_2$/100 mL NH_3.
[c] 1.3 mol $NaNH_2$/100 mL NH_3.
[d] α,α-Bis(1,4-dimethoxy-2-naphthyl)acetonitrile also obtained in 9% yield.
[e] α,α-Bis(1,4-dimethoxy-2-naphthyl)acetonitrile also obtained in 20% yield.
[f] α,α-Bis(1,4-dimethoxy-2-naphthyl)acetonitrile (**4j**), yield 49%.
[g] 9-Aminophenanthrene also obtained in 21% yield.
[h] 9-Aminophenanthrene also obtained in 30% yield.
[i] 9-Aminophenanthrene also obtained in 25% yield.
[j] 9-Aminophenanthrene also obtained in 28% yield.
[k] Caubere's base ($NaNH_2$/ethoxyethoxyethanol).
[l] α,α-diphenanthrylacetonitrile also obtained in 32% yield.

The reaction of **1** with alkanenitriles **2f–i** in sodium amide and liquid ammonia supplied α-(1,4-dimethoxy-2-naphthyl)alkanenitriles **4f–i** in yields of 52–79% (entries 9, 12–14), using 0.2 mol sodium amide, 0.1 mol **2f–i** and 0.05 mol **1** per 100 mL of liquid ammonia. Bis-α,α-(1,4-dimethoxy-2-naphthyl)alkanenitriles **4j–m**, arising from the addition of the initially formed anion of **4f–i** with another molecule of 1,4-dimethyl-2-naphthalyne were also obtained in smaller amounts (< 10%). Interestingly, the ratio of monoarylated (**4f**) to diarylated (**4j**) nitrile from the acetonitrile (**2f**) reactions decreased from 69:9 (entry 9) to 56:20 (entry 10) to 31:49 (entry 11), as the amount of the reactants per 100 mL of ammonia were increased 2.5 and 6.5 fold, respectively. The use of high concentrations of reactants in sodium amide–liquid ammonia mediated aryne reactions may prove useful in the preparation of α,α-diarylacetonitriles. To see if the yields of **4** could be improved using LDA, we treated **1** and acetonitrile (**2f**) with 3 equiv of LDA, and found that 1,4-dimethoxy-2-naphthylacetonitrile (**4f**) was obtained in significantly lower yield (37%) than that using sodium amide (69%). Since no synthetic advantage was gained by using the LDA–THF system as compared to the sodium amide–liquid ammonia system, the reaction of **1** with other alkanenitriles was not further investigated.

The reaction of 9-bromophenanthrene (**3**) and alkanenitriles **2f–i** with sodium amide (entries 18–21) gave the corresponding α-phenanthrylacetonitriles **5f–i** in fair yields (26–31%). The yields of **5f–i** were negatively affected by the formation of significant amounts of 9-aminophenanthrene (21–30%), which resulted from the amination of the 9-phenanthryne by the liquid ammonia solvent. Comparable yields (26–33%) of **5f–h** were obtained using LDA in THF (entries 22–24). Although only trace amounts of the aminated product 9-*N*,*N*-diisopropylaminophenanthrene were found, considerable debromination (20–30%) of **3** was observed. The use of Caubere's[6] complex base [$NaNH_2$/$Et(OCH_2CH_2)_2OH$] gave **5f** from **3** and **2f** in slightly higher yield (40%), however, appreciable amounts (32%) of α,α-diphenanthrylarylated nitrile (entry 25) was also obtained, making separation of the nitrile products difficult.

The structures of **4**, **5** and **6** were assigned on the basis of their ^1H NMR, ^{13}C NMR and MS spectra, and elemental analyses. For example, the ^1H NMR spectra of α-arylnaphthylacetonitriles **4a–d** and **5a–c** reveal singlets (1 H) around $\delta = 5.7–5.8$ corresponding to the α-hydrogen of the cyano side chain, whereas the rearranged nitriles **6b–e** feature singlets (2 H) around $\delta = 4.3$, corresponding to the methylene hydrogen atoms of the arylmethyl group. In addition, the MS spectra of the α-arylnitriles show intense P-1 *m/z* peaks, which occasionally are base peaks, indicating the loss of the α-hydrogen atom from the parent ion.

Scheme 1 describes the competing aryne and tandem addition–rearrangement mechanisms in the reaction of **3** with arylacetonitriles. As shown, α-metalated arylacetonitriles **8** add to 9,10-phenanthryne (**9**) yielding lithio- (**10b**) and sodio-adducts (**10a**), respectively. Of these, only **10b** undergoes cyclization to benzocyclobutenium species **12**, the crucial step in the tandem addition–rearrangement pathway. Ring opening of **12** yields the α-lithiated nitrile **13**, which upon proton quench is converted into rearranged nitriles **6**. The relief of unfavorable steric interactions between the peri 1-hydrogen and 9-nitrile-containing side chain provides the driving force for the cyclization of **10** to **12**.[7] A similar explanation has been proposed to account for the propensity of 1,2-naphthalyne–aryl anion adducts to yield rearrangement nitriles.[1] Based on product distributions of rearranged (to aryne) arylated nitriles, the propensity of the initially formed lithiated aryne–nitrile adducts to yield rearranged nitrile products decreases along the series 9-phenanthryne > 1,2-naphthalyne > 2,3-naphthalyne. This trend varies inversely with the length of the C≡C bond of the aryne



Scheme 1

precursor,[8] suggesting that the stability of the aryne may be a measure of the tendency of arynes to give rearranged products. The sodio adducts **10a** apparently are quenched by the ammonia solvent and subsequently deprotonated by sodium amide to **11** before they can undergo the intramolecular cyclization step in the rearrangement pathway. The resulting α-arylated nitriles **11** are then converted into **5** upon final quenching with NH_4Cl. The failure of aryne–nitrile anion adducts from 2-bromo-1,4-dimethoxynaphthalene (**1**) to proceed through the rearrangement pathway may effect also the absence of a peri-hydrogen effect or a decrease in the nucleophilicity of the cyclization site in the adduct (i.e. the lithiated benzenoid carbon), brought about by the electron-withdrawing nature of the *meta* methoxy group.[9]

We currently are studying the reaction of other halogen substituted polyarenes with nitriles and various aryne-generating systems and will report the results in due course.

All reagents were purchased from Aldrich Chemical Company. The nitriles were distilled prior to use, butyllithium was used as received, and THF was freshly distilled from sodium benzophenone ketyl. IR spectra were recorded on a Perkin-Elmer 283 grating spectrophotometer. NMR spectra were recorded on a IBM-Bruker WP 200-SY spectrometer and chemical shifts were related to tetramethylsilane as an internal standard. 2-Bromo-1,4-dimethoxynaphthalene (**1**) was prepared by treating 1,4-dimethoxybenzene with *N*-bromosuccinimide in DMF at r.t. Compounds **4a, c, d, f–j, 5e–h,** and **6b–e** gave C,H,N ± 0.3%, except **4c**, H + 0.44%.

Aryne Arylation Reactions Using LDA; General Procedure:
In a flame-dried flask flushed with N_2, LDA (30 mmol) was prepared by adding diisopropylamine (20 mmol) to a solution of butyllithium (30 mmol, 2.5 M in hexane) in THF (50 mL) at − 78 °C. After stirring for 10 min, the appropriate nitrile (10 mmol) in THF (50 mL) was added dropwise over 20 min and the stirring was continued at − 78 °C. After warming to − 40 °C, the appropriate aryne precursor (**1** or **3**) (10 mmol) in THF (50 mL) was added dropwise. The resulting dark-red solution was allowed to warm to r.t. over 1 h and allowed to stir for an additional 2 h, at which point the solution was quenched with abs. EtOH, the THF was evaporated under reduced pressure, and the remaining residue was extracted with CH_2Cl (2 × 50 mL). The combined extracts were washed with brine, dried (Na_2SO_4), and concentrated (rotary evaporator) to provide an oil which was purified by flash column chromatography (silica gel; hexane/acetone, 19:1).

Aryne Arylation Reactions Using Sodium Amide; General Procedure:
To a flame-dried 300 mL flask equipped with dry-ice condenser was added 100 mL of liquid NH_3, Small pieces of Na were then added until the characteristic blue color of the ammonia solvated electron persisted for 1 min. After a small sample of $FeCl_3 \cdot (H_2O)_6$ (0.1 g) was added, the blue color was discharged, usually within 1 min, indicating the conversion of the sodium into sodium amide. The remainder of the Na (a total of 1.94 g, 0.08 mol) was added, and the mixture was stirred until the discharge of the blue color occurred (usually within 5 min). The nitrile (0.04 mol), dissolved in 10 mL of dioxane, was added dropwise over 5 min, the resulting solution was stirred an additional 10 min, and the halopolyarene (0.02 mol), dissolved in 10 mL of dioxane, was added dropwise over 3 min. The mixture was then stirred for 30 min, quenched with excess NH_4Cl (53 g), the ammonia was removed by heating with a steam bath, and the remaining residue was extracted with CH_2Cl_2 (2 × 50 mL). The combined methylene extracts were treated in the same manner as that described above in the LDA-mediated reactions.

α-Phenyl-1,4-dimethoxy-2-naphthylacetonitrile (**4a**):
Colorless crystals; mp 122–123 °C.

^{1}H NMR ($CDCl_3$): δ = 3.96 (s, 3H), 3.97 (s, 3H), 5.70 (s, 1H), 7.36–7.63 (m, 7H), 8.09 (dd, *J* = 7.5, 2.0 Hz, 1H), 8.29 (dd, *J* = 7.5, 2.0 Hz, 1H).

^{13}C NMR: δ = 36.09, 55.71, 62.72, 102.71, 122.14, 122.66, 123.78, 126.18, 126.75, 127.18, 127.45, 127.99, 128.14, 128.99, 135.61, 146.82, 152.74.

α-(3-Methoxyphenyl)-1,4-dimethoxynaphthylacetonitrile (**4c**):
Colorless crystals; mp 137–139 °C.

^{1}H NMR ($CDCl_3$): δ = 3.80 (s, 3H), 3.96 (s, 3H), 5.87 (s, 1H), 6.69 (s, 1H), 6.87 (d, *J* = 7.0 Hz, 1H), 7.01–7.07 (m, 2H), 7.30 (dd, *J* = 7.0 Hz, 1H), 7.58–7.61 (m, 2H), 8.08 (d, *J* = 9.5 Hz, 1H), 8.27 (d, *J* = 9.5 Hz, 1H).

^{13}C NMR: δ = 36.01, 55.23, 55.71, 62.72, 102.67, 113.24, 113.51, 119.75, 119.84, 122.14, 122.66, 123.66, 126.18, 126.75, 128.14, 130.00, 127.03, 146.83, 152.71, 160.04.

α-(3,4-Dimethoxyphenyl)-1,4-dimethoxynaphthylacetonitrile (**4d**):
Colorless crystals; mp 116–118 °C.

1,4-Dimethoxy-2-naphthylacetonitrile **(4f)**:

Colorless crystals (EtOAc); mp 106–108 °C.

^{1}H NMR ($CDCl_3$): δ = 3.92 (s, 2H), 3.94 (s, 3H), 4.01 (s, 3H), 6.74 (s, 1H), 7.57–7.61 (m, 3H), 8.04 (dd, J = 8.4, 1.6 Hz, 1H), 8.28 (dd, J = 8.4, 1.6 Hz, 1H).

^{13}C NMR ($CDCl_3$): δ = 18.33, 55.65, 62.05, 103.44, 118.02, 118.14, 121.69, 122.53, 125.87, 126.45, 127.06, 128.14 147.13, 152.40.

α-(Methyl)-1,4-dimethoxy-2-naphthylacetonitrile **(4g)**:

Colorless viscous liquid.

^{1}H NMR ($CDCl_3$): δ = 1.71 (d, J = 7.2 Hz, 3H), 3.96 (s, 3H), 4.05 (s, 3H), 4.53 (q, J = 7.2 Hz, 1H), 6.82 (s, 1H), 7.52–7.60 (m, 2H), 8.03 (dd, J = 6.7, 1.5 Hz, 1H), 8.28 (dd, J = 6.7, 1.5 Hz, 1H).

α-(Ethyl)-1,4-dimethoxy-2-naphthylacetonitrile **(4h)**:

Colorless viscous liquid.

^{1}H NMR ($CDCl_3$): δ = 1.14 (t, J = 7.3 Hz, 3H), 1.96–2.16 (m, 2H), 3.94 (s, 3H), 4.03 (s, 3H), 4.33 (t, J = 7.5 Hz, 1H), 6.77 (s, 1H), 7.51–7.59 (m, 2H), 8.03 (dd, J = 7.7, 1.5 Hz, 1H), 8.27 (dd, J = 7.7, 1.5 Hz, 1H).

^{13}C NMR: δ = 11.84, 28.26, 32.70, 55.71, 62.57, 102.06, 121.24, 121.94, 122.55, 123.69, 125.87, 126.45, 127.03, 128.15, 146.58, 152.56.

α-(Propyl)-1,4-dimethoxy-2-naphthylacetonitrile **(4i)**:

Colorless viscous liquid.

^{1}H NMR ($CDCl_3$): δ = 1.01 (t, J = 7.3 Hz, 3H), 1.50–2.13 (m, 4H), 3.95 (s, 3H), 4.04 (s, 3H), 4.39 (t, J = 8.7 Hz, 1H), 6.79 (s, 1H), 7.52–7.60 (m, 2H), 8.03 (dd, J = 8.3, 1.5 Hz, 1H), 8.27 (dd, J = 8.3, 1.5 Hz, 1H).

α,α-Bis(1,4-Dimethoxy-2-naphthyl)acetonitrile **(4j)**:

Colorless crystals (EtOAc); mp 150–152 °C.

^{1}H NMR ($CDCl_3$): δ = 3.92 (s, 6H), 4.00 (s, 6H), 6.42 (s, 1H), 6.95 (s, 2H), 7.54–7.61 (m, 4H), 8.07–8.12 (m, 2H), 8.27–8-32 (m, 2H).

^{13}C NMR ($CDCl_3$): δ = 31.33, 55.77, 62.35, 103.13, 120.12, 128.39, 147.12, 152.49, 152.49.

9-Phenanthrylacetonitrile **(5e)**:

Colorless crystals; mp 51–53 °C.

^{1}H NMR ($CDCl_3$): δ = 3.98 (s, 2H), 7.5–7.85 (m, 7H), 8.60–8.80 (m, 2H).

α-Methyl-9-phenanthrylacetonitrile **(5f)**:

Colorless viscous liquid.

^{1}H NMR ($CDCl_3$): δ = 1.75 (d, J = 9.0 Hz, 3H), 4.55 (q, J = 9.0, 1H), 7.65–7.05 (m, 7H), 8.60–8.80 (m, 2H).

α-Ethyl-9-phenanthrylacetonitrile **(5g)**:

Colorless viscous liquid.

^{1}H NMR ($CDCl_3$): δ = 1.75 (d, J = 9.0 Hz, 3H), 4.55 (q, J = 9.0, 1H), 7.65–7.05 (m, 7H), 8.60–8.80 (m, 2H).

α-Propyl-9-phenanthrylacetonitrile **(5h)**:

Colorless viscous liquid.

^{1}H NMR ($CDCl_3$): δ = 0.97 (t, J = 9.0 Hz, 3H), 1.26–2.25 (m, 4H), 4.52 (t, J = 8.5, 1H), 7.60–7.95 (m, 7H), 8.55–8.80 (m, 2H).

10-(4-Methoxyphenyl)-9-phenanthrenecarbonitrile **(6b)**:

Colorless crystals; mp 155–158 °C.

^{1}H NMR ($CDCl_3$): δ = 3.75 (s, 3H), 4.81 (s, 2H), 6.80 (d, J = 8.7 Hz, 2H), 7.17 (d, J = 8.7 Hz, 2H), 7.61–7.79 (m, 4H), 8.16 (d, J = 7.8 Hz, 1H), 8.35–8.44 (m, 1H), 8.69–8.78 (m, 2H).

10-(3-Methoxyphenyl)-9-phenanthrenecarbonitrile **(6c)**:

Colorless crystals; mp 126–127 °C.

^{1}H NMR ($CDCl_3$): δ = 3.70 (s, 3H), 4.83 (s, 2H), 6.73–6.85 (m, 3H), 7.15–7.44 (m, 5H), 8.13–8.16 (m, 2H), 8.73–8.78 (m, 2H).

10-(3,4-Dimethoxyphenyl)-9-phenanthrenecarbonitrile **(6d)**:

Colorless crystals; mp 80–82 °C.

^{1}H NMR ($CDCl_3$): δ = 3.76 (s, 3H), 3.77 (s, 3H), 4.70 (s, 2H), 6.66 (s, 1H), 6.80 (d, J = 8.7 Hz, 1H), 7.17 (d, J = 8.7 Hz, 2H), 7.61–7.79 (m, 3H), 8.16 (d, J = 7.8 Hz, 1H), 8.35–8.44 (m, 1H), 8.69–8.78 (m, 2H).

10-(3,4,5-Trimethoxyphenyl)-9-phenanthrenecarbonitrile **(6e)**:

Colorless crystals; mp 118–120 °C.

^{1}H NMR ($CDCl_3$): δ = 3.88 (s, 3H), 3.83 (s, 6H), 3.80 (s, 2H), 6.82 (s, 2H), 7.65–7.05 (m, 6H), 8.60–8.80 (m, 2H).

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