Available online at www.sciencedirect.com

SCIENCE DIRECT®

Tetrahedron 60 (2004) 3797–3802

Tetrahedron

Reaction of 1,8-diaminonaphthalene with some selected π-acceptors; prospective optically active non-linear cyanovinylated naphthalenes as well as synthesis of novel perimidin and pleiadene derivatives

Ashraf A. Aly* and Kamal M. El-Shaieb

Department of Chemistry, Faculty of Science, El-Minia University, El-Minia 61519, Egypt

Received 3 December 2003; revised 6 February 2004; accepted 4 March 2004

Abstract—Reactions of 1,8-diaminonaphthalene with some selected π-acceptors are reported herein. The reaction of the 1,8-diaminonaphthalene with 1,1,2,2-tetracyanoethylene (TCNE) and 7,7′,8,8′-tetracyanoquinodimethane (TCNQ), via different modes of cyanovinylation, yielded (2*E*)-2,3-bis-(8-aminonaphthalen-1-ylamino)-but-2-enedinitrile and 2-[4-(1*H*,3*H*-perimidin-2-ylidene)cyclohexa-2,5-dienylidene]malononitrile, respectively. On the other site, the reaction of the target molecule with 2-dicyanomethyleneindane-1,3-dione (CNIND), 2-(2,4,7-trinitro-9*H*-fluoren-9-ylidene)propane-dicarbonitrile (DTF) and 2,3-dichloro-4,5-dicyano(2,3,4,5-tetrachloro)-1,4-benzoquinones (DDQ and CHL-*p*) afforded perimidin and pleiadene derivatives.

---

1. Introduction

In spite of 1,8-diaminonaphthalene (**1**) having bidenate nucleophilic centers, limited studies have been reported on the utilization of **1** in the field of heterocyclic synthesis.[1–4] On the other site, most of the chemistry of **1** has been directed towards metal complexes.[5–7] Reactions of aromatic amines with 1,1,2,2-tetracyanoethylene (TCNE) and 7,7′,8,8′-tetracyanoquinodimethane (TCNQ) afforded tricyanovinylated products, which are known as second-order optically active non-linear compounds.[8,9] This is rationalized by the principle that chromophores comprising electron donor (D) linked to electron acceptor (A) by means of a conjugated π-electron system have non-linear optical activities. The utility of non-linear optical (NLO) phenomena underpins many operations performed by devices in telecommunication systems switching nodes and provide a means for optical signal processing in general. Therefore, we examined the reactions of **1** with both TCNE and TCNQ, on one site. We also investigated the reaction of **1** with other selected π-acceptors aiming to obtain heterocyclic compounds which might have biological and/or pharmaceutical applications.

Sometime ago, we reported an anomalous behavior for 4-amino[2.2]paracyclophane and its *N*-methyl derivative towards TCNE and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), that led to unexpected products such as 2-(4-[2.2]paracyclophanyl)-3,3-dicyanoxaziridine, 4-(*N*-carbonitrile-*N*-ethyl)amino-[2.2]paracyclophane as well as 2,3-dichloro-5-cyano-6-([2.2]paracyclophanyl)amino-1,4-benzoquinone.[10] We also isolated tricyanovinylated products during the reaction of TCNE with amines derived by heterocyclic compounds.[11,12] Moreover, we succeeded in the syntheses of many heterophanes and heterocycles.[13–15] We also synthesized 1,4-benzoxazepines by the reaction of 4-arylidene-2-phenyl-5(4*H*)-1,3-oxazolones with benzyne via [2π+2π]cycloaddition.[16] Subsequently, we examined the reaction of *N*-vinyl-1*H*-imidazole with 1,2-dehydrobenzene and some selected π-deficient compounds which was catalytic under basic conditions,[17] and we showed the effects of microwaves and thermolysis on the cyclization of thiourea derivatives.[18]

2. Results and discussion

In the light of the aforementioned promising results, our attention was turned to study the reaction of compound **1** with various π-acceptors (see Fig. 1). The reactivity **1** towards 1,1,2,2-tetracyanoethylene (TCNE, **2**), 7,7′,8,8′-tetracyanoquinodimethane (TCNQ, **4**), 2-dicyanomethyleneindane-1,3-dione (CNIND, **6**), 2-(2,4,7-trinitro-9*H*-fluoren-9-ylidene)propane-dicarbonitrile (DTF, **8**), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, **10**) and

---

Keywords: 1,8-Diaminonaphthalene; π-Acceptors; Cyanovinylation; Perimidines; Pleiadenes.

* Corresponding author. Tel.: +2086346876; fax: +2086346876; e-mail address: ashraf160@yahoo.com

0040–4020/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2004.03.017

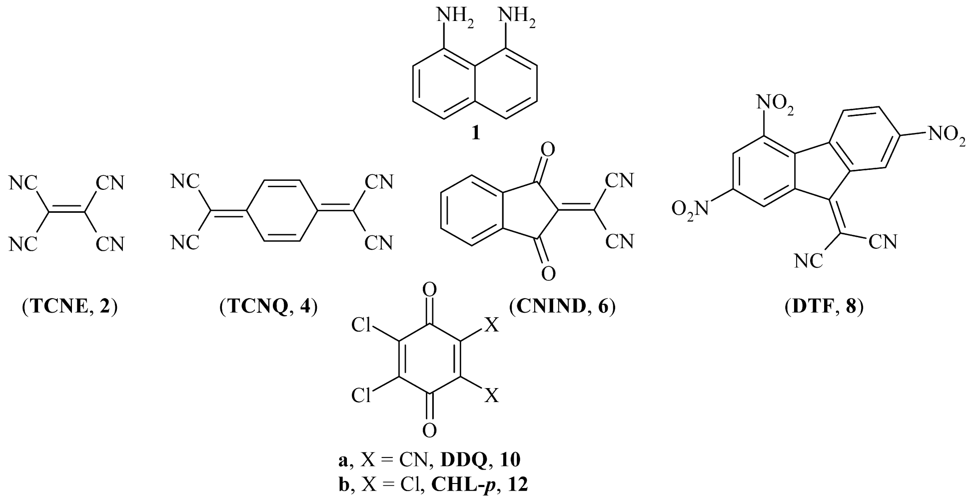
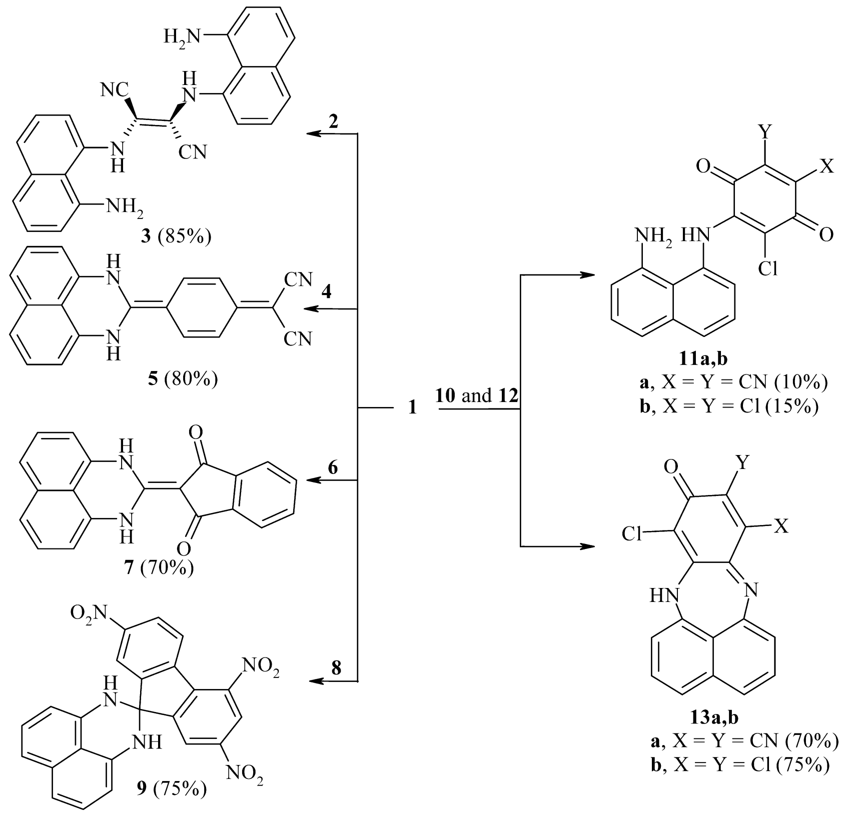


Figure 1.

2,3,5,6-tetrachloro-1,4-benzoquinone (CHL-*p*, **12**) is outlined in Scheme 1. It is interested to note that the reactions of **1** with the aforementioned π-acceptors were carried out in dry ethyl acetate at −15 °C under N_2 atmosphere. Addition of **1** as an electron donor to electron acceptors in dichloromethane at −15 °C leads to complex formation characterized by CT-bands in the visible region (Table 1). These CT-complexes gradually disappeared to give the precipitated reaction products. Presumably, CT-complexes exist as transient steps before chemical reactions have taken place. The reaction time and the λ_{max} of the CT-complexes of **1** with the former acceptors are given in Table 1.

Upon treatment of compound **2** (TCNE, Fig. 1) with **1**, under the reaction conditions mentioned before, the reaction afforded compound **3** in 85% yield (Scheme 1). The structural proof of **3** was based upon the mass, ^{1}H NMR, ^{13}C NMR and IR spectra as well as elemental analysis. Mass spectroscopy and elemental analysis proved the molecular formula of **3** as $C_{24}H_{18}N_6$. The IR spectrum of **3** revealed broad absorption bands at ν_{max} 3220–3180 (NH, NH_2) and 2218 (CN) cm^{-1}. The NH-proton resonated in the ^{1}H NMR spectrum of **3** at δ_H 11.80 (2H), whereas the NH_2 appeared at δ_H 3.90 (4H), which indicated that the cyanovinylation process occurs on one NH_2 in each of molecule of **1**. The symmetrical structure of **3** was confirmed, since its ^{1}H NMR



Scheme 1. Reaction of **1** with some selected π-acceptors.

Table 1. Reaction time and absorption maxim for the CT-complexes of **1** towards various π-acceptors in dichloromethane at −15 °C

Acceptor	λ_{max} (nm)	Reaction time (h)	Acceptor	λ_{max} (nm)	Reaction time (h)
2	500	1	**8**	420	2
4	470	3	**10**	520	4
6	440	2.5	**12**	400	6

spectrum showed six discernible sets of aromatic protons, which appeared as multiplets and the others as double-doublets, each set related to two protons. The ^{13}C NMR spectrum proved the ^{1}H NMR spectroscopic data by the appearance of only 12-carbon signals. The COSY H–H and C–H spectra of **3** indicated some distinctive δ values as given in Figure 2. According to semi-empirical calculations using the MM2 level of theory,[19] the stereoview of compound **3** (Scheme 1), in the case of minimization the steric energy value, is in its *E*-form (ΔH_f=196.98 kcal/mol) rather than in the *Z*-form (ΔH_f=314.90 kcal/mol). It is therefore suggested that the structure of **3** was identified as (2*E*)-2,3-bis-(8-aminonaphthalen-1-ylamino)-but-2-enedinitrile.

7,7′,8,8′-Tetracyanoquinodimethane (TCNQ, **4**, Fig. 1) has attracted interest because its cyanovinylated products have non-linear optical properties.[8,20] Interest in organic light emitting chromophores has expanded rapidly since the discovery of efficient electro-luminescence (EL), its use in light emitting devices and its potential for electrically pumped solid state lasers.[8,20] In an attempt to carry out the reaction of **1** with **4**, under the same reaction conditions as between **1** and **2**, the reaction produced compound **5** in 80% yield (Scheme 1). The IR, ^{1}H NMR, ^{13}C NMR and mass spectra as well as elemental analysis confirmed the structural feature of **5**. The molecular formula of **5** was elucidated by mass spectroscopy and elemental analysis as $C_{20}H_{12}N_4$. The ^{1}H NMR spectrum of **5** is in accordance with the suggested structure and showed three multiplets (6H), two double-doublets (4H) and a broad singlet (2H). The ^{13}C NMR of **5** confirmed its ^{1}H NMR spectral data by the appearance of thirteen carbon signals, which indicated its symmetry. The COSY H–H and C–H spectra of **5** showed most of distinctive δ values of **5** as given in Figure 2. Compound **5** was unequivocally identified as 2-[4-(1*H*,3*H*-perimidin-2-ylidene)cyclohexa-2,5-dienylidene]malononitrile.

Interestingly, the reaction between **1** and 2-dicyanomethyleneindane-1,3-dione (CNIND,[21] **6**, Fig. 1) yielded another class of symmetrical perimidin derivative **7** in 70% yield (Scheme 1). Elemental analysis as well as IR, ^{1}H NMR, ^{13}C NMR and mass spectra established the structural proof of **7**. Elemental analysis and mass spectra confirmed the molecular formula of **7** as $C_{20}H_{12}N_2O_2$. The IR spectrum of **7** showed NH and carbonyl absorption bands at ν_{max} 3180 and 1690 cm^{-1}, respectively. It was clearly noted in the IR spectrum of **7** that there is no absorption due to the nitrile-group. The ^{1}H NMR spectrum of **7** revealed the NH-proton at δ_H 11.60 (2H) related to the NH-protons. The symmetrical structure of **7** was elucidated by ^{13}C NMR spectrum, since only 12 carbon signals were recognized. The COSY H–H and C–H spectra of **7** demonstrated some distinctive δ values as given in Figure 2. By the help of the obtainable spectral data, compound **7** was identified as 2-(1*H*,3*H*-perimidin-2-ylidene)-indan-1,3-dione.

Surprisingly, the reaction of **1** with 2-(2,4,7-trinitro-9*H*-fluoren-9-ylidene)propane-dicarbonitrile (DTF,[22] **8**, Fig. 1) afforded the spiro-heterocyclic compound **9** in 75% yield (Scheme 1). The latter reaction occurred by elimination of a molecule of malononitrile from **8**. The IR spectrum of **9** did not show any absorption due to the nitrile group, whereas a strong band appeared at ν_{max} 3180 cm^{-1} related to the amino group. The ^{1}H NMR spectrum of **9** revealed two apparent double-doublets at δ_H 6.00 and 6.30 (*J*=8.6, 1.4 Hz), each integrating for one proton, corresponding to the naphthalene molecule (Fig. 2). Additionally, H-3 and

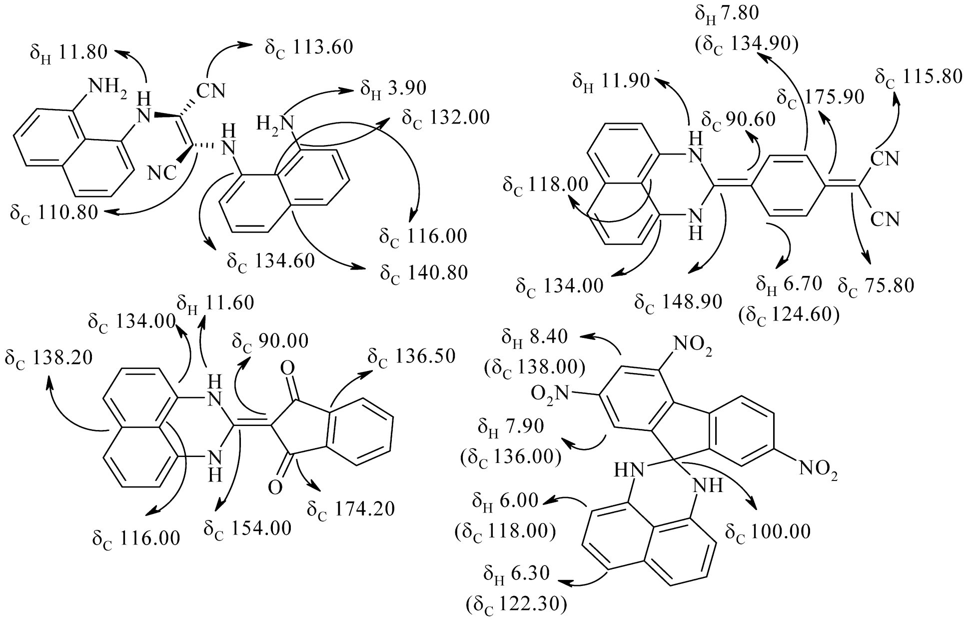


Figure 2. Distinctive chemical shifts (δ s) of compounds **3**, **5**, **7** and **9**.

H-1 were resonated in the ^{1}H NMR spectrum of **9** as two doublets at δ_H 8.40 and 7.90 (J=2.0 Hz), respectively. Moreover, the two NH-protons were appeared in the ^{1}H NMR spectrum of **9** at δ_H 3.90 and 3.94. The ring-current effect of the fluorenyl ring was previously studied.[23] It was shown that the fluorenyl ring system seems to be less aromatic because it contains a 5-membered ring with 4π-electrons.[23] Thus, the presence of the electron-withdrawing groups on the benzene rings of fluorenyl group will reduce the electron density on C-9. However, the presence of the electron-donating groups attached to C-9 will increase the aromaticity of the fluorenyl rings, as it allows donation of electron density into the 'empty' π-atomic orbital of C-9.[23] Thus, the two former factors affect the shielding and/or the deshielding appearance of C-9. Since, the withdrawing effect of the nitro-groups is expected to proceed over the donating effect of the NH– groups, this can explain the deshielding appearance of C-9 in compound **9** (δ_C 100.00). Moreover, COSY H–H and NOE spectra of **9** indicated some distinctive δ values as given in Figure 2 (see also Section 3).

The reactions of **1** with π-acceptors (**2**, **4**, **6** and **8**, Fig. 1) proceeded by nucleophilic addition of the NH groups of **1** to the π-deficient double bonds, followed by elimination. On reacting **1** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, **10**) and 2,3,5,6-tetrachloro-1,4-benzoquinone (CHL-*p*, **12**), the reaction performed by elimination to give **11a**,**b**, which was followed by condensation to afford products **13a**,**b** (Scheme 1). We found that compounds **13a**,**b** were obtained in higher percentage yields compared with **11a**,**b** (Scheme 1). The ability to separate side products of **11a** or **11b** indicated that addition-elimination sequence preceded the condensation. The structural proof of compounds **11a**,**b** and **13a**,**b** was made on the basis of elemental analyses as well as IR, ^{1}H NMR, ^{13}C NMR and mass spectra. For example mass spectroscopy and elemental analysis confirmed the molecular formula of **13a** as $C_{18}H_7ClN_4O$. The IR spectrum of **13a** demonstrated strong absorption bands at ν_{max} 3180, 1690 and 2218 cm^{-1} related to the absorptions of amine–NH, carbonyl and cyano groups, respectively. The ^{1}H NMR spectrum of **13a** revealed a broad singlet at δ_H 11.82, whereas two double-doublets (J=8.0, 1.2 Hz) and two multiplets could be also distinguished, which were attributed to naphthalene protons. The ^{13}C NMR spectrum of **13a** showed its unsymmetrical structure, since all carbons in the molecular formula were accounted. Four remarkable signals were distinguished in the ^{13}C NMR of **13a** at δ_C 170.00, 155.80, 113.80 and 113.92 corresponding to carbonyl-, azomethine- and two nitrile-carbons. The proposed structure of **13a** and **13b** were identified as 11-chloro-10-oxo-10,12,12a,12b-tetrahydro-7,12-diaza-pleiadene-8,9-dicarbonitrile and 8,10,11-trichloro-6a,12b-dihydro-7*H*-7,12-diaza-pleiaden-9-one.

In conclusion, our results demonstrated for the first time, a general, methodology for the construction of a variety of little investigated types of heterocyclic compounds (pleiadene and perimidin) due to the difficulties accompanied their synthesis. We can also utilize by our target molecule in a promised synthesis of other interest heterocyclic compounds.

3. Experimental

Melting points are uncorrected. IR spectra were obtained on Shimadzu 470 spectrophotometer using potassium bromide pellets. ^{1}H NMR (400.134 MHz) and ^{13}C NMR (100.6 MHz) spectra were measured on Bruker AM 400 with TMS as an internal standard. Coupling constants are expressed in Hz. Mass spectra were recorded on a Finnigan MAT 8430 instrument at 70 eV. Elemental analyses were carried out in the Microanalysis Center of the Institut für Anorganische Chemie, Technische Universität Braunschweig. For preparative thin layer chromatography (PLC), glass plates (20×48 cm) were covered with slurry of silica gel Merck PF_{254} and air-dried using the solvents listed for development.

3.1. Starting materials

Commercial 1,8-diaminonaphthalene (**1**) was used from Fluka. 1,1,2,2-Tetracyanoethylene (TCNE, **2**), 7,7′,8,8′-tetracyanoquinodimethane (TCNQ, **4**), 2-dicyanomethyleneindane-1,3-dione (CNIND, **6**), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, **10**) and 2,3,5,6-tetrachloro-1,4-benzoquinone (CHL-*p*, **12**) were bought from Merck. 2-Dicyanomethyleneindane-1,3-dione (CNIND, **6**), and 2-(2,4,7-trinitro-9*H*-fluoren-9-ylidene)propanedicarbonitrile (DTF, **8**) were prepared following the procedure mentioned in refs. 21 and 22, respectively. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, **10**) and 2,3,5,6-tetrachloro-1,4-benzoquinone (CHL-*p*, **12**) were bought from Aldrich.

3.2. General procedure. Reaction of 1 with 2, 4, 6, and 8. General procedure

In an ice-salt bath (−15 °C), a solution of **1** (0.16 g, 1 mmol) in dry ethyl acetate (20 mL) was added dropwise to a solution of the acceptor **2**, **4**, **6**, or **8** (2 mmol) in dry ethyl acetate (50 mL) under N_2 atmosphere over 10 min. The reaction mixture was further stirred at the former temperature for 1–3 h (Table 1) until the consumption of the starting materials was completed (the reaction progress was monitored by TLC analysis). The solvent was evaporated under vacuum and the residue was applied on PC using toluene as eluent. The major zones were recrystallized from the stated solvents.

3.2.1. (2*E*)-2,3-Bis-(8-aminonaphthalen-1-ylamino)-but-2-enedinitrile (3). Compound **3** (0.38 g, 85%) as green crystals (R_f 0.3, CH_2Cl_2), mp 160–162 °C (acetonitrile); [Found: C, 73.70; H, 4.58; N, 21.46 requires $C_{24}H_{18}N_6$ (390.440): C, 73.83; H, 4.65; N, 21.52%]; ν_{max} (KBr) 3220–3180 (NH, NH_2), 3030–2985 (Ar-CH), 2218 (CN), 1590 (C=N) cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 400 (3.90); δ_H (DMSO-d_6) 3.90 (4H, br s, 2NH_2), 6.60 (2H, dd, J=8.4, 1.6 Hz), 7.20–7.36 (2H, m), 7.40 (2H, dd, J=8.4, 1.4 Hz), 7.50–7.66 (2H, m), 7.80 (2H, dd, J=8.4, 1.4 Hz), 8.00–8.18 (2H, m), 11.80 (2H, br s, NH); δ_C (DMSO-d_6) 110.80 (vinyl-*C*), 113.60 (CN), 116.00 (naph-*C*), 127.90, 128.80, 129.20, 131.20, 131.60 (naph-CH), 132.00 (naph-*C*–NH_2), 133.00 (naph-CH), 134.60 (naph-*C*–NH), 140.80 (naph-*C*); *m*/*z* (%) 390 [M$^+$] (100), 232 (46), 206 (18), 180 (22), 168 (20), 154 (24), 140 (16), 106 (22), 92 (24), 78 (16), 50 (12), 24 (14).

3.2.2. 2-[4-(1*H*,3*H*-Perimidin-2-ylidene)cyclohexa-2,5-dienylidene]malononitrile (5). Compound **5** (0.25 g, 80%) as orange crystals (R_f 0.5, CH_2Cl_2), mp 180–182 °C; [Found: C, 77.75; H, 3.90; N, 18.16 requires $C_{20}H_{12}N_4$ (308.350): C, 77.91; H, 3.92; N, 18.17%]; ν_{max} (KBr) 3210 (NH), 3045–2990 (Ar-CH), 2220 (CN), 1590 (C=N) cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 420 (4.00); δ_H ($CDCl_3$) 6.40–6.60 (2H, m, naph-H), 6.70 (2H, dd, *J*=8.5, 1.4 Hz, quinone-CH), 7.56–7.74 (2H, m, naph-H), 7.80 (2H, dd, *J*=8.4, 1.5 Hz, quinone-CH), 7.90–8.08 (2H, m, naph-H), 11.90 (2H, br s, NH); δ_C ($CDCl_3$) 75.80 [=*C*(CN)$_2$], 90.60 (*C*=C–NH), 115.80 (CN), 118.00 (naph-*C*), 124.60 (quinone-CH), 126.60, 128.80 (naph-CH), 129.90 (naph-*C*), 133.00 (naph-CH), 134.00 (naph-*C*–NH), 134.90 (quinone-CH), 136.90 (naph-*C*), 148.90 (*C*-3), 175.90 (*C*=C(CN)$_2$); *m/z* (%) 308 [M$^+$] (100), 282 (20), 256 (24), 244 (32), 168 (18), 132 (16), 104 (20), 92 (18), 78 (20), 50 (16).

3.2.3. 2-(1*H*,3*H*-Perimidin-2-ylidene)-indan-1,3-dione (7). Compound **7** (0.22 g, 70%) as orange crystals, (R_f 0.4, CH_2Cl_2), mp 260–262 °C (ethanol); [Found: C, 76.75; H, 3.90; N, 8.80 requires $C_{20}H_{12}N_2O_2$ (312.322): C, 76.91; H, 3.87; N, 8.97%]; ν_{max} (KBr) 3180 (NH), 3045–2990 (Ar-CH), 1690 (CO), 1590 (C=N), 1580 (C=CH) cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 400 (3.90); δ_H ($CDCl_3$) 6.40–6.56 (2H, m, naph-H), 6.90 (2H, dd, *J*=8.4, 1.4 Hz), 7.40–7.60 (2H, m, naph-H), 7.80–8.00 (2H, m, Ar-H), 8.10–8.14 (2H, m, naph-H), 11.60 (2H, br s, NH); δ_C ($CDCl_3$) 90.00 (C=*C*–CO), 116.00 (naph-*C*), 126.00 (2C, naph-CH), 128.00 (2C, Ar-CH), 128.90 (2C, naph-CH), 130.86 (2C, Ar-CH), 132.00 (2C, Ar-*C*), 133.60 (2C, naph-CH), 134.00 (2C, naph-*C*–NH), 138.20 (naph-*C*), 154.00 (*C*-2), 174.20 (2C, *C*=O); *m/z* (%) 312 [M$^+$] (100), 282 (54), 258 (18), 220 (18), 180 (22), 156 (34), 144 (24), 126 (26), 78 (16).

3.2.4. 2,9-Spiro-[2,4,7-trinitro-fluorene]-1*H*,3*H*-perimidin-2-ylidene (9). Compound **9** (0.35 g, 75%) as yellow crystals (R_f 0.2, ethyl acetate), mp >300 °C (acetone); [Found: C, 60.50; H, 2.80; N, 15.20 requires $C_{23}H_{13}N_5O_6$ (455.379): C, 60.66; H, 2.88; N, 15.38%]; ν_{max} (KBr) 3180 (NH), 3060–3010 (Ar-CH), 1590 (C=N), 1568 (C=CH), 1320–1350 (Ar-NO_2 stretch) cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 360 (3.62); δ_H (DMSO-d_6) 3.90 (1H, br s, NH), 3.94 (1H, br s, NH), 6.00 (1H, dd, *J*=8.6, 1.4 Hz, naph-H), 6.30 (1H, dd, *J*=8.6, 1.4 Hz, naph-H), 6.40–6.60 (4H, m, naph-H), 7.40–7.68 (3H, m, Ar-H), 7.90 (1H, d, *J*=2.0 Hz, H-1), 8.40 (1H, d, *J*=2.0 Hz, H-3); δ_C (DMSO-d_6) 100.00 (*C*-9), 118.00, 122.30, 124.80, 126.90, 128.60 (naph-CH), 128.80 (naph-*C*), 128.90 (naph-CH), 130.00, 132.00, 132.40 (naph-*C*), 133.00, 133.20, 133.40, 133.60 (Ar-*C*), 134.00, 134.20, 135.22 (Ar-CH), 136.00 (CH-1), 138.00 (CH-3), 146.80, 147.00, 147.80 (Ar-*C*–NO_2); *m/z* (%) 456 [M+1] (30), 455 [M$^+$] (100), 408 (20), 362 (16), 328 (26), 316 (20), 212 (18), 166 (32), 120 (24), 104 (22), 50 (16), 24 (18).

3.3. Reaction of 1 with 10 and 12. General procedure

By applying the same procedure mentioned before, a solution of either **10** or **12** (2 mmol) in dry ethyl acetate (50 mL) was added dropwise to **1** (0.16 g, 1 mmol) in dry ethyl acetate (20 mL) under N_2 atmosphere in 30 min. The reaction mixture was stirred at the former temperature for 1 h and at room temperature for 3–5 h (Table 1). The solvent was then removed under vacuum and the residue was applied on PLC using toluene: ethyl acetate as eluent (5:1). In case of the reaction of **1** with either **10** or **12**, the first migrating zone contained compounds **11a**,**b**, whereas the second migrating one contained compounds **13a**,**b**.

3.3.1. 4-(8-Aminonaphthalen-1-ylamino)-5-chloro-3,6-dioxo-cyclohexa-1,4-diene-1,2-dicarbonitrile (11a). Compound **11a** (0.04 g, 10%) as pale yellow crystals (R_f 0.6, CH_2Cl_2), mp >300 °C (ethyl acetate); [Found: C, 61.80; H, 2.55; Cl, 10.00, N, 16.16 requires $C_{18}H_9ClN_4O_2$ (348.743): C, 61.99; H, 2.60; Cl, 10.17; N, 16.07%]; ν_{max} (KBr) 3230–3210 (NH,NH_2), 3045–2990 (Ar-CH), 2220–2210 (CN), 1690 (CO), 1585 (C=N) cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 340 (3.20); δ_H (DMSO-d_6) 4.00 (2H, br s, NH_2), 6.20–6.40 (2H, m, naph-H), 6.70–7.10 (3H, m), 7.92–8.10 (1H, m), 11.40 (1H, br s, NH); δ_C (DMSO-d_6) 114.50, 115.80 (CN), 120.00 (*C*-5), 122.40 (naph-*C*), 126.60, 126.80, 128.24, 130.20, 132.00, 132.18 (naph-CH), 134.00 (naph-*C*–NH_2), 135.60, 135.90 (*C*-1 and *C*-2), 137.00 (naph-CH), 138.00 (naph-*C*), 141.80 (naph-*C*–NH), 170.00, 172.00 (*C*-3 and *C*-6); *m/z* (%) 348 [M$^+$] (100), 346 (30), 316 (20), 290 (24) 288 (26), 274 (18), 220 (24), 178 (20), 150 (16), 134 (24), 104 (18), 92 24), 78 (18), 24 (14).

3.3.2. 2-(8-Aminonaphthalen-1-ylamino)-3,5,6-trichloro-1,4-benzoquinone (11b). Compound **11b** as pale yellow crystals (0.06 g, 15%), (R_f 0.5, CH_2Cl_2), mp >300 °C (ethanol); [Found: C, 52.40; H, 2.40; Cl, 28.80; N, 7.52 requires $C_{16}H_9Cl_3N_2O_2$ (367.613): C, 52.28; H, 2.47; Cl, 28.93; N, 7.62%]; ν_{max} (KBr) 3225–3210 (NH,NH_2), 3045–2990 (Ar-CH), 1690 (CO), 1592 (C=N) cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 325 (3.10); δ_H (DMSO-d_6) 3.90 (2H, br s, NH_2), 6.18–6.40 (2H, m, naph-H), 6.58–7.00 (3H, m), 7.80–7.94 (1H, m), 11.60 (1H, br s, NH); δ_C (DMSO-d_6) 113.30, 113.60, 114.20 (*C*-3, *C*-5 and *C*-6), 118.90 (naph-*C*), 124.50, 125.90, 128.20, 130.00, 132.20, 132.24 (naph-CH), 134.10 (naph-*C*–NH_2), 136.00 (naph-CH), 137.20 (naph-*C*), 140.00 (naph-*C*–NH), 170.20, 172.60 (*C*-3 and *C*-6); *m/z* (%) 378 [M$^+$] (100), 376 (86), 374 (44), 372 (14), 342 (34), 316 (20), 304 (24), 280 (24), 278 (28), 220 (24), 178 (20), 150 (16), 134 (24), 104 (18), 92 (24), 78 (18), 50 (18), 24 (14).

3.3.3. 11-Chloro-10-oxo-10,12,12a,12b-tetrahydro-7,12-diaza-pleiadene-8,9-dicarbonitrile (13a). Compound **13a** as yellow crystals (0.23 g, 70%), (R_f 0.2, CH_2Cl_2), mp 286–288 °C (acetone); [Found: C, 65.55; H, 2.08; N, 16.80 requires $C_{18}H_7ClN_4O$ (330.727): C, 65.37; H, 2.13; N, 16.94%]; ν_{max} (KBr) 3180 (NH), 3050–2996 (Ar-CH), 2218 (CN), 1690 (CO), 1590 (C=N) cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 410 (3.68); δ_H (DMSO-d_6) 6.50 (1H, dd, *J*=8.4, 1.4 Hz, naph-H), 7.20–7.50 (3H, m, naph-H), 7.70 (1H, dd, *J*=8.4, 1.4 Hz, naph-H), 8.00–8.12 (1H, m, naph-H), 11.82 (1H, br s, NH); δ_C (DMSO-d_6) 113.00 (*C*-11), 120.80 (naph-*C*), 113.80, 113.92 (CN), 126.40, 128.00, 130.14, 130.50, 132.50, 134.00 (naph-CH), 134.60 (naph-*C*–NH_2), 135.20, 135.68 (*C*-8 and *C*-9), 137.80 (naph-*C*–NH), 138.00 (naph-*C*), 138.60 (naph-*C*–N), 155.80 (*C*=N), 170.00 (*C*-10); *m/z* (%) 330 [M$^+$] (100), 328 (34), 296 (20), 272 (22), 244 (30), 172 (20), 132 (18), 104 (22), 88 (16), 50 (12), 24 (14).

3.3.4. 8,10,11-Trichloro-6a,12b-dihydro-7*H*-7,12-diazapleiaden-9-one (13b). Compound **13b** as yellow crystals (0.27 g, 75%), (R_f 0.3, CH_2Cl_2), mp 260–262 °C (acetone); [Found: C, 54.80; H, 2.00; N, 8.10 requires $C_{16}H_7Cl_3N_2O$ (349.598): C, 54.97; H, 2.02; N, 8.01%]; ν_{max} (KBr) 3220 (NH), 3065–3000 (Ar-CH), 1680 (CO), 1590 (C=N) cm^{-1}; UV (CH_3CN) λ_{max} (log ε) 350 (3.40); δ_H (DMSO-d_6) 6.30 (1H, dd, *J*=8.4, 1.6 Hz, naph-H), 7.00–7.38 (3H, m, naph-H), 7.65 (1H, dd, *J*=8.6, 1.5 Hz, naph-H), 7.90–8.00 (1H, m, naph-H), 11.80 (1H, br s, NH); δ_C (DMSO-d_6) 113.00, 113.60, 114.20 (*C*-8, 10 and 11), 120.40 (naph-*C*), 126.00, 126.90, 128.26, 130.00, 132.00, 132.90 (naph-CH), 133.80 (quinone-*C*–NH), 135.80 (naph-*C*–NH), 136.40 (naph-*C*), 138.00 (naph-*C*–N), 155.00 (*C*=N), 170.20 (*C*-9); *m*/*z* (%) 349 [M^+] (100), 347 (80), 345 (42), 343 (16), 316 (28), 314 (30), 280 (12), 278 (16), 244 (14), 242 (18), 192 (20), 176 (16), 142 (20), 88 (26), 50 (12), 24 (14).

References and notes

1. Koutentis, P. A.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1999**, 111–117.
2. Ozeryanskii, V. A.; Filatova, E. A.; Sorokin, V. I.; Pozharskii, A. F. *Russ. Chem. Bull.* **2001**, *50*, 854–855.
3. Clayden, J.; Westlund, N.; Frampton, C. S. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1379–1385.
4. Shvekhgeimer, M.-G. A. *Chem. Heterocycl. Compd.* **2001**, *37*, 385–443.
5. Cabeza, J. A.; Noth, H.; Rosales-Hoz, M. de J.; Sanchez-Cabrera, G. *Eur. J. Inorg. Chem.* **2000**, 2327–2332.
6. Nachtigal, C.; Al-Gharabli, S.; Eichele, K.; Lindner, E.; Mayer, H. A. *Organometallics* **2002**, *21*, 105–112.
7. Clegg, W.; Horsburgh, L.; Mulvey, R. E.; Rowlings, R. *Chem. Commun.* **1996**, 1739–1740.
8. Szablewski, M.; Thomas, P. H.; Thornton, A.; Bloor, D.; Cross, G. H.; Cole, J. M.; Howard, J. A. K.; Malagoli, M.; Meyers, F.; Bredas, J.-L.; Wenseleers, W.; Goovaerts, E. J. *J. Am. Chem. Soc.* **1997**, *119*, 3144–3154.
9. Miller, J. S. *Extended linear chain compounds*; Plenum: New York, 1983; Vols. 1–3. pp 981–1001. (b) Ferraro, J. R.; Williams, J. M. *Introduction to synthetic electrical conductors*; Academic: San Diego, CA, 1987.
10. Aly, A. A.; Hassan, A. A.; Mourad, A. E. *Can. J. Chem.* **1993**, *71*, 1845–1849.
11. Mourad, A. E.; Hassan, A. A.; Mohamed, N. K.; Aly, A. A.; Bahaa, A. A. *Heterocycl. Commun.* **2001**, *7*, 541–548.
12. Hassan, A. A.; Mohamed, N. K.; Aly, A. A.; Mourad, A. E. *Pharmazie* **1997**, *52*, 23–28.
13. Aly, A. A. *Tetrahedron* **2003**, *59*, 1739–1747.
14. Aly, A. A. *Org. Biomol. Chem.* **2003**, *1*, 756–761.
15. Aly, A. A.; Mourad, A. E.; Hassan, A. A.; Mohamed, N. K.; Ali, B. A.; El-Sayed, M. M. *Arch. Pharm. Pharm. Med. Chem.* **2004**, *337*, 133–139.
16. Aly, A. A. *Tetrahedron* **2003**, *59*, 6067–6073.
17. Aly, A. A. *Eur. J. Org. Chem.* **2004** under publication.
18. Hassan, A. A.; Mourad, A. E.; El-Shaieb, K. M.; Abou-Zeid, A. H.; Döpp, D. *Heteroatom* **2003**, *14*, 535–541.
19. Allinger, N. L. *MM2 (91) force field Program, obtained from Quantum Chemistry Program*; Indiana University; *Molecular Mechanics PM3 Program (ACD/3D)*, Advanced Chemical Development Inc.: Toronto, Canada, 1988.
20. Boor, D.; Kagawa, Y.; Szablewski, M.; Ravi, M.; Clark, S. J. *J. Mater. Chem.* **2001**, *11*, 3053–3062.
21. Chatterjee, S. *J. Chem. Soc. B* **1969**, 725–730.
22. Mukherjee, T. K.; Levasseur, L. A. *J. Org. Chem.* **1965**, *30*, 644–646.
23. (a) Komatsu, K.; Takimoto, N.; Murata, Y.; Wan, T. S. M. *Tetrahedron Lett.* **1996**, *37*, 6153–6156. (b) Murata, Y.; Komatsu, K.; Wan, T. S. M. *Tetrahedron Lett.* **1996**, *37*, 7061–7064. (c) Okamura, H.; Murata, Y.; Minoda, M.; Komatsu, K.; Miyamoto, K.; Wan, T. S. M. *J. Org. Chem.* **1996**, *61*, 8500–8502. (d) Murata, Y.; Ito, M.; Komatsu, K. *J. Mater. Chem.* **2002**, *12*, 2009–2020.