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Syntheses, Electrochemistry and Molecular Modeling of N,N'-Dicyanoquinonediimine (DCNQI) Derivatives of Substituted 1,4-Anthracenediones: Precursors for Organic Metals.

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Abstract: The title compounds (**10**) have been obtained from the corresponding 1,4-anthracenedione derivatives (**3**), prepared by different synthetic routes, by reaction with bis(trimethylsilyl)carbodiimide (BTC). The cyclic voltammetry of these compounds (**3** and **10**) reveals the presence of two reduction waves to the corresponding anion-radical and dianion. The acceptor ability of compounds **10** can be modulated by the presence of substituents on the DCNQI ring. The *syn/anti* isomers have been studied by molecular mechanics and the results are in good agreement with the ^{1}H-NMR high resolution spectral data.

INTRODUCTION

N,N'-Dicyanoquinonediimine (DCNQI) and its derivatives, first reported by Hünig *et al.*[1] have proved to be a very important class of electron acceptors able to form ellectrically conducting charge transfer complexes (CTC) and charge transfer salts.[2] The acceptor strength of DCNQI is comparable to that of tetracyano-*p*-quinodimethane (TCNQ). In fact, whereas the copper salt of 2,5-dimethyl-DCNQI showed a conductivity of 5.10^5 S.cm^{-1} at 3.5 K, the analogous $(TCNQ)_2Cu$ salt resulted to be only a semiconductor.[3] Depending on the nature of the substituents, some copper salts of 2,5-substituted DCNQI derivatives retain metallic behaviour at very low temperatures, while others undergo a metal to insulator transition due to the deformation of the tetrahedral coordination around the copper.[4]

On the other hand, the structural study of 9,10-anthraquinone DCNQI derivatives showed a considerably more planar geometry than the corresponding TCNQ derivatives.[5]

Very recently, we have reported the synthesis, electrochemistry and crystal structure of DCNQI derivatives containing fused benzene rings on both 2,3 and 5,6 positions, and discussed their acceptor ability in terms of steric and electronic effects.[6] The influence of the substituents on the DCNQI system to tune the electron affinity and the effect of the π-extension to reduce the intramolecular Coulomb repulsion[7] are interesting structural modifications to form highly conducting CTC.

In this paper we present the synthesis and electrochemistry of novel DCNQI derivatives from 2,3-substituted 1,4-anthraquinones in which the π-extension in the DCNQI system is achieved by 5,6-fused aromatic rings. The geometry of this type of acceptors should present a better planarity than the previously described 2,3-5,6 benzene fused DCNQI derivatives.[1,6] Additionally, the presence of a variety substituents in 2,3-positions on the DCNQI moiety, allows to tune the acceptor ability of the novel molecules.

RESULTS AND DISCUSSION

The synthesis of the novel π-extended DCNQI derivatives have been carried out from the corresponding substituted 1,4-anthracenediones by reaction with *bis*-(trimethylsilyl)carbodiimide (BTC) according to Hünig's method.[1]

There is not a general procedure for the introduction of different substituents on 2,3- and 6,7-positions in the 1,4-anthracenedione system and, consequently, we have followed three very different synthetic routes (A, B, C) to obtain these quinones as is depicted in the Scheme 1.

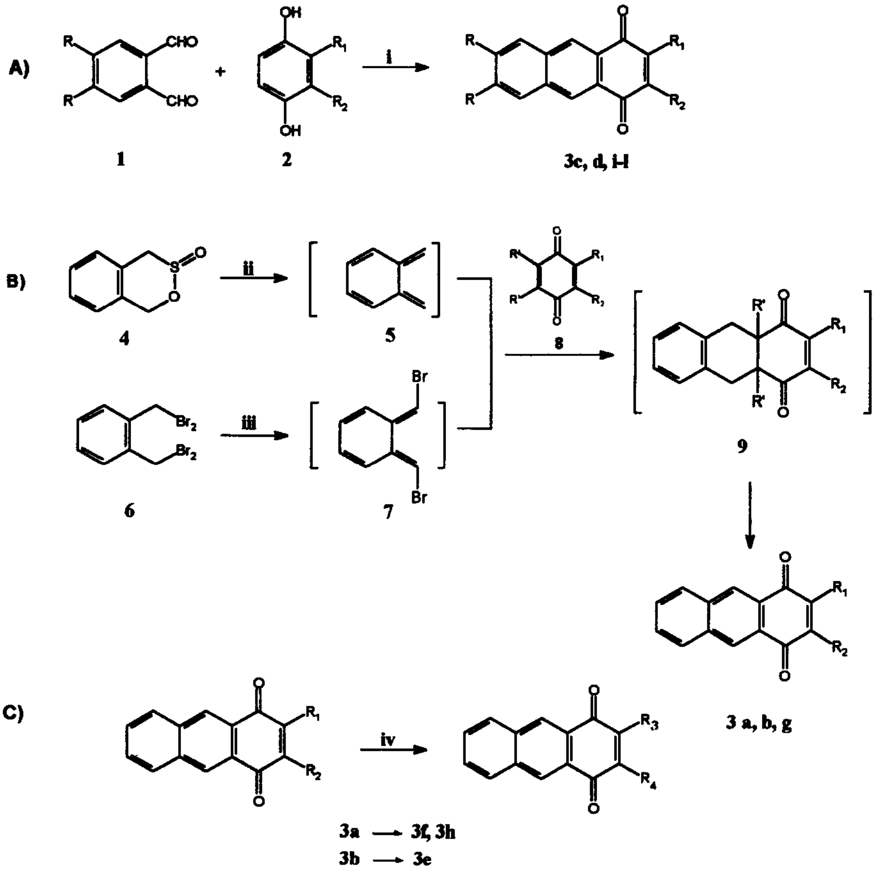
Route A leads to substituted 1,4-anthracenediones by reaction of symmetrically substituted phtaldialdehydes **1**[8] with 2,3-substituted hydroquinones **2** in 1,1,1-trifluoroethanol by following the procedure described by Lepage.[9] The scope of this method is limited as it requires the presence in R_1 and R_2 of activating groups. Thus, reaction of phtaldialdehyde derivatives [**1**, R=H, OMe, $-(CH=CH)_2$] with 2-methoxyhydroquinone **2** (R_1=OMe; R_2=H) and 2,3-dimethylhydroquinones **2** (R_1=R_2=Me) led to the corresponding 1,4-anthraquinone derivatives **3** (**c**,**d**,**i**-**l**) in good yields. Reaction with 2-methylhydroquinone (**2**, R_1=Me; R_2=H) led to the corresponding 2-methyl-1,4-anthraquinone in very low yield. Finally, reaction with 2,3-dicyano-*p*-hydroquinone, in which the ring bears two deactivating cyano groups, does not take place. The various substituted 1,4-anthracenediones obtained by this procedure are listed in the Table 1.

Table 1. Substituted 1,4-anthracenediones 3 obtained.

Compound	Route	R	R_1	R_2	R_3	R_4	Yield(%)[a]
3a	B	H	H	H	-	-	Ref. 14
3b	B	H	Me	H	-	-	40
3c	A	H	OMe	H	-	-	90
3d	A	H	Me	Me	-	-	Ref. 9
3e	C	H	-	-	Me	Br	80
3f	C	H	-	-	Cl	H	Ref. 21
3g	B	H	Br	Br	-	-	44
3h	C	H	-	-	Cl	Cl	Ref. 13
3i	A	OMe	Me	Me	-	-	54
3j	A	$-(CH=CH)_2-$	Me	Me	-	-	51
3k	A	OMe	OMe	H	-	-	93
3l	A	$-(CH=CH)_2-$	OMe	H	-	-	80

[a] Yields are given in isolated product.

To overcome the difficulties of the route A, we followed the route B. By reaction of substituted *p*-benzoquinones **8** with the highly reactive *o*-quinodimethanes[10] (**5**,**7**) generated favorably either from sultine **4**[11] or from α,α,α',α'-tetrabromo-*o*-xylene **6**[12], 1,4-antracenediones **3a, b, g** were easily obtained in moderate yields (see Table 1). The intermediate Diels-Alder adduct **9** easily undergoes oxydation to the fully aromatized quinone **3**.



i. Na_2CO_3, CF_3CH_2OH, ii. C_6H_6, reflux; iii. NaI, DMF, iv (**3a-3f, 3h**) Cl_2, AcOH, reflux; (**3b-3e**) Br_2, pyridine, CH_3CN

Scheme 1

Finally, a third route (C) in which 1,4-anthracenediones **3** were obtained, in one step from other substituted 1,4-anthracenediones as starting materials was also used. Thus, bromination of 2-methyl-1,4-anthracenedione **3b** led, in good yield, to the corresponding 2-methyl-3-bromo-1,4-anthracenedione **3e**. The 2-chloro-1,4-anthracenedione **3f** and 2,3-dichloro-1,4-anthracenedione **3h** were obtained from the unsubstitued 1,4-anthracenedione **3a** by chlorination with chlorine gas. Compound **3h** was not described spectroscopically in the literature[13] and now these data are presented in the experimental section.

The different substituted 1,4-anthracenediones derivatives are listed in Table 1 together with the followed experimental procedure.

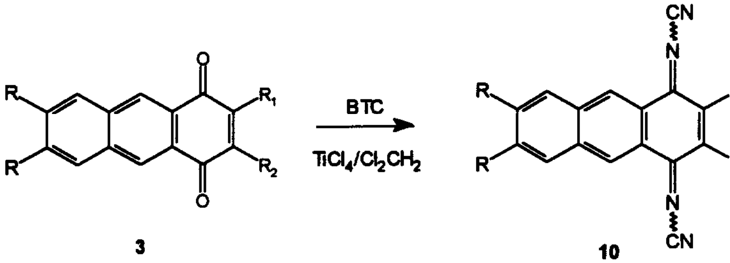
N,N'-Dicyanoquinonediimine (DCNQI) derivatives **10** were finally synthesized from the substituted 1,4-anthracenediones **3** by reaction with BTC[15] and titanium tetrachloride in methylene dichloride as the solvent (Scheme 2). Compounds **10** were thus obtained as stable orange or red solids in moderate to good yields (see Table 2). These compounds **10** exist as the corresponding *syn* and *anti* isomers.

In order to gain energetic insight as an aid for distinguishing between the *syn/anti* isomers for cyano groups, MMX molecular mechanics[16] analyses of **10b** and **10g** were undertaken considering all the possible relative orientations for cyano groups. Table 3 summarizes the energies for the 4 possible isomers of **10b**.

Table 2. N,N'-Dicyanoquinonediimine (DCNQI) Derivatives **10** Prepared.

Compound	R	R_1	R_2	Yield(%)^a
10a	H	H	H	Ref. 2
10b	H	Me	H	80
10c	H	OMe	H	54
10d	H	Me	Me	54
10e	H	Me	Br	75
10f	H	Cl	H	80
10g	H	Br	Br	60
10h	H	Cl	Cl	71
10i	OMe	Me	Me	44

^{a}Yields are given in isolated product



Scheme 2

A comparative analysis of the energetic terms in table 3 indicates that different stabilities between A, D and B, C can be accounted for mainly by differences in stretching and Van der Waals terms. A similar minimum value of energy has been found for isomers A and D (Figure 1), indicating that the cyano group on the N atom in position 1 should isomerize at room temperature. However, minimization shows that in the monosustituted cyanoimine **10b** the cyano group on the N atom in position 4 should has a stable *anti* configuration in relation to the ring. The difference of energy between B or C, where the CN group is *syn* respecting to the ring, and A or D, where is *anti*, is higher than 3 Kcal/mol.

Table 3. Result of MMX Molecular Mechanics calculations [a] for **10b**[17]

isomer	E_T	E_{str}	E_{bnd}	$E_{s\text{-}b}$	E_{tor}	E_{vdw}	$E_{q\text{-}q}$
A	55.4	1.0	3.6	0.1	19.3	13.9	17.5
B	60.3	1.2	6.8	0.1	19.3	14.8	18.1
C	58.5	1.0	5.2	0.1	19.3	14.3	18.6
D	55.2	0.9	2.6	0.1	19.3	13.2	19.1

[a] Energies are in Kcal/mol. E_T is the sum of the following terms: E_{str}, bond stretching energy; E_{bnd} ,bending energy; $E_{s\text{-}b}$, stretch-bend energy; E_{tor}, torsional energy; E_{vdw}, van der Waals energy; $E_{q\text{-}q}$, polar interactions energy.

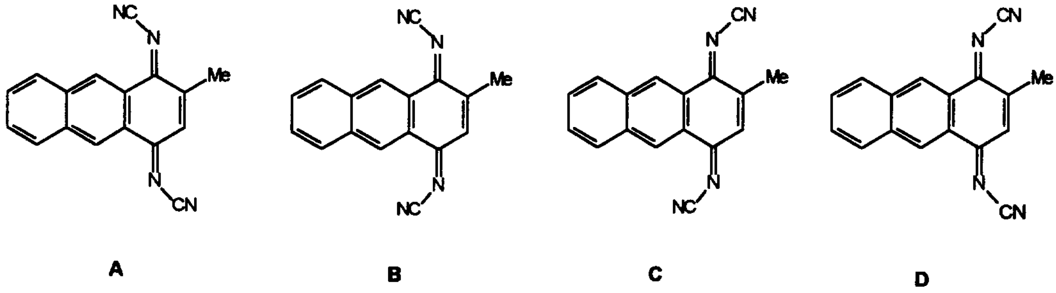


Figure 1

The lowest energy isomer for dibromoderivative **10g** (*anti/anti*) is depicted in figure 2. The small difference (1.2 Kcal) between the energy of the *anti/anti* isomer (79.7 Kcal/mol) and the *syn/anti* isomer (80.9 Kcal/mol) supports the idea of the fast isomerization of both =N-CN groups; the less stable isomer is the *syn/syn* isomer (83.5 kcal/mol). Molecular mechanics indicates that these N,N'-dicyanoquinonediimines derivatives **10** are nearly planar. Even the presence of two bromine atoms do not disturb the planarity of the molecule, all of the diedral angles being smaller than 2°.

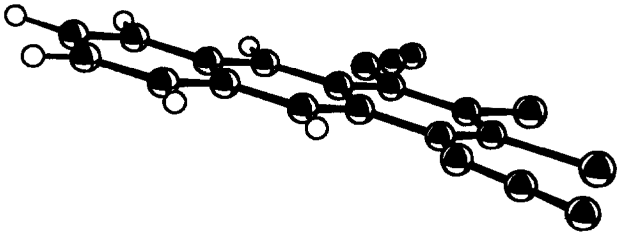


Figure 2. ORTEP estereoview of the minimum energy structure of **10g**

The high resolution ^{1}H-NMR spectra of monosubstituted DCNQI derivatives **10** (R_2=H) exhibited two different signals for the aromatic hydrogens H_a and H_b close to the cyanoimine groups (Figure 3). Thus, proton H_a appears at a lower field as a broad singlet due to the rapid isomerization at room temperature.

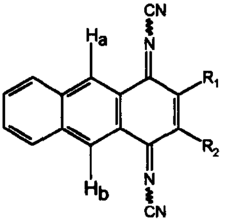


Figure 3

The steric hindrance of the substituent R_1 and the *peri* hydrogen H_a leads to a no significant difference in energy towards a favoured configuration and, consequently, the observed signal appears as a broad singlet. On the other hand, the presence of a hydrogen atom in R_2 results in a stable configuration of the neighbouring cyanoimine group and, accordingly, a singlet is observed for the *peri* hydrogen H_b. (Figure 3).

When two substituents other than hydrogen (R_1,R_2≠H) are present simultaneously in the molecule **10**, there is not a favoured stable configuration and the *peri* hydrogens H_a and H_b in **10** appear as a broad singlet. These results are in good agreement with the molecular mechanics calculations.

The CV measurements of the novel compounds were carried out in acetonitrile at room temperature with tetrabutylammonium perchlorate as the supporting electrolyte. The half-wave redox potentials of the DCNQI derivatives **10** together with those of their precursor quinones (**3**) are summarized in Table 4. For comparison purposes, the CV measurement of the parent DCNQI, in the same experimental conditions, is also included.

All the N,N'-dicyanoimino derivatives showed two one-electron reversible reduction waves to the corresponding anion-radicals and dianions. This is in good agreement with the results found recently for the larger π-extended polycyclic systems.[6] However, the decreasing benzannulation in compounds **10** results in more positive reduction potentials (Table 4). It has been proved that poorer reduction potentials result when benzannulation is increased due, mainly, to steric factors.[18] The first reduction potential of the N,N'-dicyano-1,4-anthraquinonediimine **10a** is, therefore tuned by the presence of different substituents in R_1 and R_2. Thus, better acceptor abilities were obtained with substituents such as chlorine or bromine (compounds **10f**, **10g**, **10h**).

The CV data indicate that compounds **10** are slighly poorer electron-acceptors than DCNQI. However, the smaller difference between the midpoint potentials for the first and second reduction of DCNQI derivatives **10** compared with that for the parent DCNQI, suggests a reduction of the intramolecular Coulomb repulsion due to the π-system extension.

The thermodynamic stabilities of the corresponding anion-radicals have been determined from the difference between the first and second reduction potentials (ΔE) by using the log K values.[19]

Table 4. Cyclic voltammetry data of novel acceptors (V *vs* SCE)

Compound	$E^1_{1/2}$ [a]	$E^2_{1/2}$	ΔE	log K [b]
3a	-0.57	-1.13	0.56	9.49
3b	-0.70	-1.26	0.56	9.49
3c	-0.73	-1.23	0.50	8.47
3d	-0.64	-1.16	0.52	8.81
3e	-0.57	-1.15	0.58	9.83
3f	-0.48	-1.04	0.55	9.65
3g	-0.31	-0.88	0.57	9.66
3h	-0.42	-0.90	0.48	8.13
3i	-0.72	-1.20	0.48	8.13
3j	-0.82	-1.25	0.43	7.28
3k	-0.74	-1.24	0.50	8.47
3l	-0.72	-1.20	0.48	8.13
DCNQI	+0.08	-0.44	0.52	8.81
10a	-0.13	-0.64	0.50	8.47
10b	-0.17	-0.62	0.45	7.62
10c	-0.12	-0.53	0.41	7.06
10d	-0.17	-0.53	0.36	6.10
10e	-0.11	-0.48	0.37	7.96
10f	-0.09	-0.55	0.46	6.27
10g	-0.05	-0.42	0.37	6.27
10h	-0.06	-0.47	0.41	7.06
10i	-0.12	-0.45	0.33	5.59

[a] Versus Ag wire as a Ag/Ag^+ quasireference electrode; electrolyte $Bu4N^+ClO4^-$; solvent Me-CN; scan rate 20mV/s.
[b] $\log K = \Delta E/ 0.058$

It has been found that the thermodynamic stability in these anion-radicals of DCNQI derivatives **10** is dependent of the substitution degree in positions 2 and 3 (R_1, R_2) and independent of the electronic nature of such substituents. Thus, the steric factors are responsable of this behaviour and, consequently, the tetrasubstitued compounds **10** ($R_1,R_2 \neq H$) exhibited a lower value of K (log K= 5.5-6.2) than the unsubstituted parent compound **10** ($R_1= R_2=H$) (log K= 8.4). (See Table 4).

As expected, a similar behaviour was found in the starting quinones **3** which also showed two one-electron reduction waves but shifted toward more negative values. As shown in Table 4, substitution on C-6 and C-7 in the 1,4-anthracenedione system has practically no effect on the first reduction potentials in these quinones (**3i-l**).

The substituent effect in positions 2 and 3 on the redox potentials of the N,N'-dicyano-1,4-anthraquinonediimines **10** serie can be correlated with the Hammett's σ constants (Figure 4). The Hammett plot of $E^1_{1/2}$ *vs.* σ_3[20] gives a ρ value of 0.123 with a correlation coefficient of $r = 0.971$. The comparison of the ρ value in this serie with the one indicated by Hünig[18] for simpler DCNQI series ($\rho= 0.490$) indicates that the substituent effect over the ease of reduction decrease as the conjugation is extended.

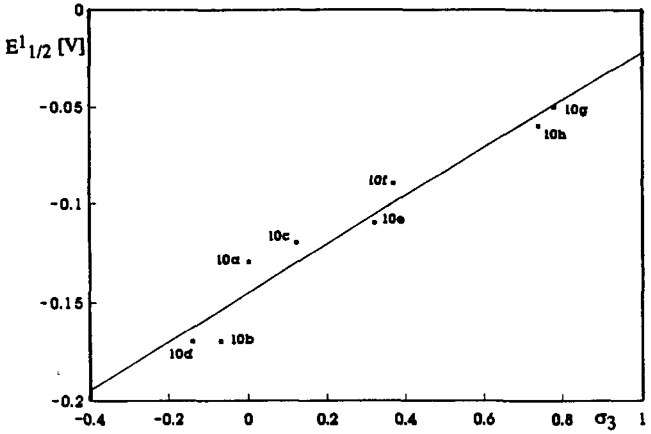


Figure 4. Hammett plot of $E^1_{1/2}$ [V] for N,N'-dicyano-1,4-anthraquinone-diimines **10** *vs.* σ_3

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EXPERIMENTAL

Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 398 and FIR spectra in a Bruker IFs 114c spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were determined with a Varian XL-300S spectrometer and elemental analyses were performed on a Perkin-Elmer CHN 2400 apparatus. Mass spectra were determined with a Varian MAT 711 spectrometer.

Cyclovoltammetric measurements were performed on a EG & G PAR Versastat potentiostat using 250 Electrochemical Analysis software. A Metrohm 6.084.C10 glassy carbon electrode was used as indicator electrode in voltammetric studies.

Phtaldialdehyde, hydroquinone, 2-methoxyhydroquinone, 2,3-dimethylhydroquinone, 2-methoxy-*p*-benzoquinone, tetrabromo-*p*-benzoquinone, α,α,α',α'-tetrabromo-*o*-xylene, sodium hydroxymethanesulfinate (Rongalite©), α,α'-dichloro-*o*-xylene, 3,4-dimethoxybenzoic acid and bis-(trimethylsilyl)carbodiimide (BTC) were commercially available.

Synthesis of substituted 1,4-anthraquinones 3. *General Procedures.*

Route A: To a solution of the corresponding phtaldialdehyde (**1**) (15 mmol) in *ca.* 20 ml of trifluoroethanol, the corresponding hydroquinone (**2**) (15 mmol) and sodium carbonate (3.2 g, 30 mmol) were added. The reaction mixture was refluxed for a variable time (24-48 h) and followed by TLC until the starting dialdehyde (**1**) was exhausted. The solid that precipitated was collected by filtration at room temperature and washed with water. Further purification was accomplished by recrystallization in the appropriate solvent.

Compounds **3a**[14] and **3d**[9] were obtained according to previously reported procedures.

2-Methoxy-1,4-anthracenedione **3c**: This compound was obtained by following the above experimental procedure in 90 % yield. M.p.(°C): 212-214 (from MeOH). IR (KBr): 3050, 2900, 1675, 1650, 1600, 1450, 1400, 1290, 1170 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 3.94 (3H, s, MeO), 6.29 (1H, s, =CH), 7.67 (2H, m, ArH), 8.03 (2H, m, ArH), 8.59 (1H, s, ArH), 8.67 (1H, s, ArH). Anal. Calcd. for $C_{15}H_{10}O_3$: C, 75.63; H, 4.20. Found: C, 75.27; H, 4.00.

6,7-Dimethoxy-2,3-dimethyl-1,4-anthracenedione **3i**: This compound was obtained by following the route A in 64 % yield. M.p. (°C): 307-309 (from Me-CN). IR (KBr): 1650, 1610, 1590, 1515, 1480, 1440, 1400, 1300, 1260 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 2.2 (6H, s, 2 x Me), 4.0 (6H, s, 2 x MeO), 7.22 (2H, d, ArH), 8.38 (2H, s, ArH). Anal. Calcd. for $C_{20}H_{16}O_4$: C, 75.00; H, 5.00. Found: C, 74.98; H, 4.99.

2,3-Dimethyl-1,4-naphthacenedione **3j**: This compound was obtained by following route A in 51 % yield. M.p. (°C): 308-310 (from DMF). IR (KBr): 1655, 1610, 1545, 1450, 1420, 1370, 1300, 1250 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 2.17 (6H, s, 2 x Me), 7.89 (2H, m, ArH), 8.58 (2H, m, ArH), 8.63 (2H, s, ArH), 8.79 (2H, s, ArH).

2,6,7-Trimethoxy-1,4-anthracenedione **3k**: This compound was obtained by following route A in 93 % yield. M.p. (°C): > 330 (from hexane-chloroform). IR (KBr): 3050, 2900, 1670, 1630, 1600, 1590, 1420, 1400, 1220 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 3.93 (3H, s, MeO), 4.05 (6H, s, 2 x MeO), 6.22 (1H, s, =CH), 7.28-7.29 (2H, m, ArH), 8.41 (1H, s, ArH), 8.50 (1H, s, ArH). Anal. Calcd. for $C_{17}H_{14}O_5$: C, 68.56; H, 4.70. Found: C, 69.02; H, 4.83.

2-Methoxy-1,4-naphtacenedione **3l**: This compound was obtained by following route A in 80 % yield. M.p. (°C): > 350 (from MeOH). IR (KBr): 3050, 2950, 1680, 1650, 1600, 1450, 1300, 1200, 1180 cm^{-1}. ^{1}H-NMR (CDCl$_3$) δ: 3.97 (3H, s, MeO), 6.35 (1H, s, =CH), 7.60-7.65 (2H, m, ArH), 8.09-8.15 (2H, m, ArH), 8.67 (1H, s, ArH), 8.67 (1H, s, ArH), 8.81 (1H, s, ArH), 8.92 (1H, s, ArH). Anal. Cald. for $C_{19}H_{12}O_3$: C, 79.17; H, 4.17. Found: C, 79.72; H, 4.20.

Route B: To a solution of the corresponding p-benzoquinone (8) (2-methyl-*p*-benzoquinone and tetrabromo-*p*-benzoquinone) (4.8 mmol) in dry benzene at reflux temperature and in argon atmosphere, 1,4-dihydro-2,3-benzoxathiin-3-oxide[11] (0.54 g, 3.2 mmol) was added dropwise. The reaction mixture was refluxed for 4 h. (TLC) and after cooling at room temperature, the solvent was evaporated *in vacuo* to dryness. The yellow solid obtained was recrystallized in the appropriate solvent.

2-Methyl-1,4-anthracenedione **3b**: This compound was obtained by following route B. The purification was accomplished by flash chromatography (silica-gel, hexane:ethyl acetate, 6:1) and then recrystallized in hexane-ethyl acetate. Yield (%): 40. M.p. (°C): 142-144. IR (KBr): 3050, 2900, 1670, 1620, 1590, 1460, 1290, 1200 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.15 (3H, s, Me), 3.98 (6H, s, 2 x MeO), 6.80 (1H, s, =CH), 7.19-7.22 (2H, m, ArH), 8.32 (1H, s, ArH), 8.36 (1H, s, ArH). Anal. Calcd. for $C_{15}H_{10}O_2$: C, 87.30; H, 4.85. Found: C, 86.92; H, 4.82.

2,3-Dibromo-1,4-anthracenedione **3g**: This compound was obtained by following the route B in 44 % yield. M.p. (°C): 293-294 (from bromobenzene). IR (KBr): 3080, 1670, 1590, 1550, 1280, 1215, 870 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 7.80-7.83 (2H, q, ArH), 8.31-8.34 (2H, q, ArH), 8.75 (2H, s, ArH). M.S. m/z (%): 364 (M^+, 35), 366 (M+2, 65), 287 (60), 285 (58), 150 (100), 77 (80). Anal. Calcd. for $C_{14}H_6Br_2O_2$: C, 45.90; H, 1.64. Found: C, 45.98; H, 1.59.

Route C: Compounds **3f**[21] and **3h**[13] were obtained from **3a** by reaction with chlorine gas by following the previously described procedures.

3-Bromo-2-methyl-1,4-anthracenedione **3e**: To a solution of 2-methyl-1,4-anthracenedione (**3b**) (2 mmol) in dry acetonitrile (10 ml) in an ice-bath and argon atmosphere, a solution of bromine (1.6 g, 10 mmol) in dry acetonitrile (2 ml) and then dry pyridine (0.8 ml) in dry acetonitrile (2 ml) were added. The dark reaction mixture was stirred vigorously for 1 h, then water (20 ml) was added and stirred at room temperature for other additional 18 h. The solid that precipitated was collected by filtration and recrystallized from acetonitrile. Yield (%): 80. M.p. (°C):228-230. IR (KBr): 3080, 2920, 1670, 1600, 1540,1400, 1340, 1290, 770 cm^{-1}.^{1}H-NMR ($CDCl_3$) δ: 2.44 (3H, s, CH_3), 7.7-7.8 (2H, m,ArH), 8.05 (2H, m, ArH), 8.65 (1H, s, ArH), 8.69 (1H, s, ArH). Anal. Calcd. for $C_{15}H_9BrO_2$: C, 58.41; H, 3.93. Found:C, 57.92; H: 3.52.

N,N'-Dicyano-1,4-anthraquinonediimines **10**. *General Procedure.*

The appropriate quinone (1 mmol) was dissolved in CH_2Cl_2 (50 ml) under inert atmosphere (argon), $TiCL_4$ (5 mmol) was added dropwise. After addition of BTC (6 mmol), the reaction mixture was stirred at room temperature for 24 h. (TLC). Then, CH_2Cl_2 (50 ml) and ice/water (50 ml) were added and the mixture was shaken vigorously. The organic phase was separated, dried over $MgSO_4$, and the solvent was removed *in vacuo*. The red solid obtained was recrystalized from the suitable solvent.

N,N'-Dicyano-1,4-anthraquinonediimine **10a**: Prepared as described[2]. Yield (%): 68. M.p. (°C): 283-284.

N,N'-Dicyano-2-methyl-1,4-anthraquinonediimine **10b**: Yield (%): 80. M.p. (°C): >350° (from hexane-chloroform). IR (KBr): 3050, 2950, 2180 (=N-CN), 1600, 1550, 1530, 1450, 1300, 1250 and 760 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2,47 (3H, s, CH_3), 7.62 (1H, s, ArH), 8.07-8.13 (2H, m, ArH), 8.94 (1H, s, ArH), 9.70 (1H, br s, ArH). Anal. Calcd. for $C_{17}H_{10}N_4$: C, 75.55; H, 3.70; N, 20.79. Found: C, 76.02; H, 3.91; N, 20.20.

N,N'-Dicyano-2-methoxy-1,4-anthraquinonediimine **10c**: Yield (%): 54. M.p. (°C): > 350 (from MeCN or CH_2Cl_2-petroleum ether). IR (KBr): 1600, 1560, 1540, 1500, 1460, 1410, 1390, 1320, 1280, 1260

cm^{-1}.^1H-NMR ($CDCl_3$) δ: 4.16 (3H, s, MeO), 6.83 (1H, s, =CH), 7.73-7.76 (2H, m, ArH), 8.06-8.09 (2H, m, ArH), 8.92 (2H, s, ArH).

N,N'-Dicyano-2,3-dimethyl-1,4-anthraquinonediimine **10d:** Yield (%): 54. M.p. (°C): > 350 (from CH_2Cl_2-petroleum ether). IR (KBr): 2160, 1590, 1550, 1490, 1450, 1400, 1375, 1300, 1180 cm^{-1}.^1H-NMR ($CDCl_3$) δ: 2.42 (6H, s, 2 x Me), 7.76-7.79 (2H, m, ArH), 8.09-8.12 (2H, m, ArH), 9.50 (2H, br s, ArH).

2-Bromo-N,N'-Dicyano-3-methyl-1,4-anthraquinonediimine **10e**: Yield (%): 75. M.p. (°C): > 350 (from hexane-chloroform). IR (KBr): 3050, 2900, 2180, 1590, 1550, 1450, 1400, 1300, 1260 cm^{-1}.^1H-NMR ($CDCl_3$) δ: 2.60 (3H, s, Me), 7.82-7.85 (2H, m, ArH), 8.13-8.16 (2H, m, ArH). Anal. Calcd. for $C_{17}H_9N_4Br$: C, 58.60; H, 2.58; N, 16.01. Found: C, 58.49; H, 2.45; N, 15.82.

2-Chloro-N,N'-Dicyano-1,4-anthraquinonediimine **10f**: Yield (%): 80. M.p. (°C): > 300 (from MeCN). IR (KBr): 3050, 2180, 1600, 1570, 1555, 1530, 1460, 1310, 870 cm^{-1}.^1H-NMR ($CDCl_3$) δ: 7.81-7.86 (2H, m, ArH), 7.96 (1H, br s, ArH), 8.10-8.17 (3H, m, ArH, =CH), 8.99 (1H, s, ArH). Anal. Calcd. for $C_{16}H_7N_4Cl$: C, 66.09; H, 2.41; N, 19.28. Found: C, 65.84; H, 2.58; N, 19.09. M.S. m/z (%): 290 (M^+).

2,3-Dibromo-N,N'-Dicyano-1,4-anthraquinonediimine **10g**: Yield (%): 60. M.p. (°C): > 300 (from MeCN). IR (KBr): 2170, 1580, 1560, 1535, 1450, 1400, 1280, 1260 cm^{-1}.^1H-NMR (DMSO) δ: 7.90-7.93 (2H, m, ArH), 8.28-8.32 (2H, m, ArH), 9.31 (2H, br s, ArH). Anal. Calcd. for $C_{16}H_6N_4Br_2$: C, 46.37; H, 1.44; N, 13.53. Found: C, 46.50; H, 1.53; N, 13.48.

2,3-Dichloro-N,N'-dicyano-1,4-anthraquinonediimine **10h**: Yield (%): 71. M.p. (°C): >400 (from MeCN). IR (KBr): 2175, 1600, 1560, 1540, 1310, 1270 cm^{-1}.^1H-NMR ($CDCl_3$) δ: 7.84-7.87 (2H, m, ArH), 8.14-8.17 (2H, m, ArH), 9.43 (2H, br s, ArH). Anal. Calcd. for $C_{16}H_6N_4Cl_2$: C, 59.07; H, 1.85; N, 17.23. Found: C, 59.14; H, 1.90; N, 17.15.

N,N'-Dicyano-6,7-dimethoxy-2,3-dimethyl-1,4-anthraquinonediimine **10i**: Yield (%): 44. M.p. (°C): >400 (from Ethanol). IR (KBr): 2160, 1615, 1545, 1510, 1480, 1320, 1260 cm^{-1}.^1H-NMR ($CDCl_3$) δ: 2.38 (6H, s, 2 x Me), 4.08 (6H, s, 2 x MeO), 7.20 (2H, s, ArH), 7.35 (2H, s, ArH). Anal. Calcd. for $C_{20}H_{16}N_4O_2$: C, 69.77; H, 4.65; N, 16.28. Found: C, 69.75; H, 4.61; N, 15.78.

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