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N,*N*-bis(quinonyl)amines; synthesis and X-ray structure

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Abstract—The preparation of several symmetrical and nonsymmetrical *N*,*N*-bis(quinonyl)amines is reported. These compounds, which have two quinones separated by one amino group, were obtained by an unexpected reaction of primary or secondary substituted aminoquinones. While not nucleophilic enough to react with simple electrophiles, these aminoquinones did react with haloquinones and also with unsubstituted quinones under very mild conditions to afford diquinonylamines in average to good yields. These vinylogous quinone-imides were characterized using common spectroscopic methods as well as X-ray crystallography.

1. Introduction

A vast number of quinones with great structural divergence are provided by nature. Some of them play a major role in the redox electron-transport chains of living systems.[1–4] Thus vitamin K is identified with blood coagulation mechanism and photosynthesis, while ubiquinone and vitamin E are important factors in electron transport and oxidative phosphorylation. Simple and more complex quinonic compounds are used extensively in medicine especially as anticancer agents. Their activity stems from their special ability to undergo one electron transfer reactions thus forming reactive radicals.[5,6] The primary radical formed is always the semiquinone radical (detectable by electron paramagnetic resonance spectroscopy) which in biological systems can proceed through an intricate cascade of electron transfer to form a variety of radicals including the highly potent and cytotoxic hydroxyl radical.[7,8] Large libraries of quinones, substituted quinones, bis-quinones and polyquinones were synthesized during the last century and their properties extensively studied.[9] Their unique ability to attract electrons and thus produce stable radicals made them a desirable target in the fast growing fields of molecular electronics and organic semiconductors.[10–14] Moreover, different anion radicals of more complex quinonic compounds exhibit intense absorption in the visible or near-infrared (NIR) region. Such a property is of importance in the fields of communication devices[15] and optical storage.[16]

Many naturally occuring products as well as numerous synthetic compounds include an aminoquinone moiety in their structure.[17] The amino group is either free, substituted, or part of a fused heterocyclic ring. Many aminoquinones are involved in enzyme inhibition, DNA cross-linking, antibacterial, antifungal and anticancer activity. During recent work in our laboratory on the synthesis of ureido- and carbamato-quinones, a minor side product was isolated and proved to be a bis-quinone in which the two quinones are directly attached to the same NH group.[18] Surprisingly, and to the best of our knowledge such bis-quinones have not been previously prepared. In the present study, we describe suitable syntheses of this new type of compounds that we expect to show interesting and unique properties. We prepared both symmetrical and non-symmetrical *N*,*N*-bis-quinonyl derivatives and characterized them via analytical, spectroscopic as well as crystallographic methods.

2. Results and discussion

2.1. Synthesis

In connection with our research on quinone–amino acids conjugates,[19,20] we designed a synthesis through which the quinone and the amino acid can be bridged via a carbamate or a ureido moiety.[18] The first step was (Scheme 1) to react 2,3-dichloro-1,4-naphthoquinone (**1**) with potassium cyanate in DMSO or in DMF. A Michael-type addition reaction took place followed by elimination of KCl to afford the quinonyl isocyanate (**2**). In the second step the quinonyl-isocyanate reacted with an alcohol or an amine to yield the carbamate or the ureido products (**3**).

Upon work-up of the reaction mixtures we found that the desired products were accompanied by a minor orange colored side product. The product was isolated from the reaction mixture using column chromatography, purified by recrystallization and characterized by microanalysis, MS, ^{1}H NMR, ^{13}C NMR and FT-IR, as the 3-*N*,*N*-bis(2-chloro-1,4-naphthoquinonyl)amine (**5a**). Supportive evidence for the

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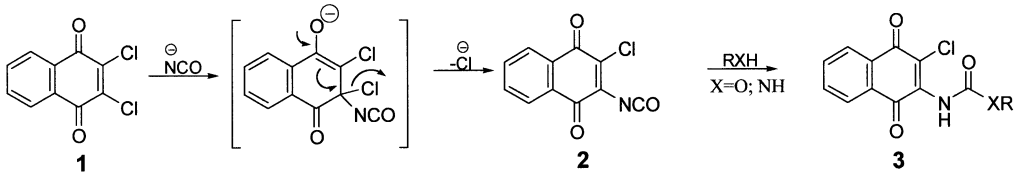
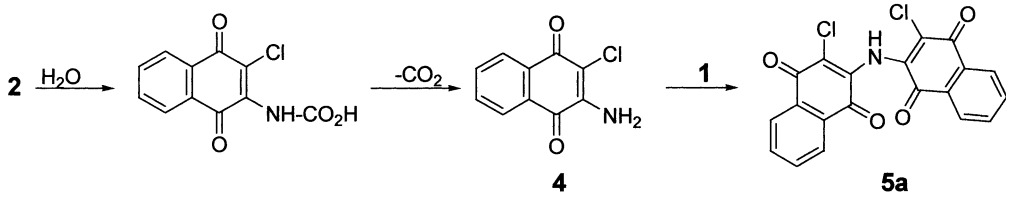


Scheme 1.



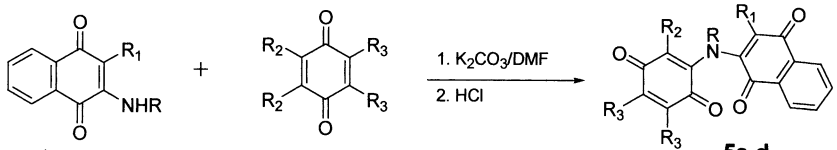
Scheme 2.

correctness of the allocated structure was obtained from X-ray analysis. It seems that partial hydrolysis of the isocyanate **2** gave the carabamic acid, which underwent spontaneous decarboxylation to yield the 2-chloro-3-amino-1,4-naphthoquinone (**4**). This aminoquinone is a vinylogous amide and thus was not expected to act as a nucleophile. However under the slightly basic reaction conditions (potassium cyanate solution) the aminoquinone did react with the starting dichloroquinone **1** and yielded the 3-*N*,*N*-bis(2-chloro-1,4-naphthoquinonyl)amine (**5a**) (Scheme 2).

In order to prove the route suggested in Scheme 2, which leads to the unexpected coupling, we prepared authentic 2-amino-3-chloro-1,4-naphthoquinone[21] and reacted 1 equiv. of it with 1 equiv. of dichloroquinone **1**, in the presence of potassium carbonate. Indeed the reaction between the two quinones proceeded at room temperature and resulted in formation of a product (58% yield), which was completely identical (physical and spectroscopic data) to the bis-quinone **5a**. Performing the same reaction in the absence of potassium bicarbonate did not produce this product indicating the importance of basic conditions. Moreover, under the same reaction conditions (room temperature, slightly basic) the aminoquinone **4** was not nucleophilic enough to undergo simple alkylation (with methyl iodide or with 2-haloketones), or even simple acylation (with acetic anhydride or acetyl chloride). This unexpected facile reaction between the two naphthoquinones is intriguing, but opened a route for the preparation of the formerly unknown bis-(quinonyl)amines. Indeed we found that this new reaction is general (Scheme 3) and primary or secondary aminoquinones can react with various haloquinones to yield the appropriate bis-(quinonyl)amines. The haloquinone might be a chloro- or bromoderivative of naphthoquinone as well as a chloro derivative of benzoquinone.

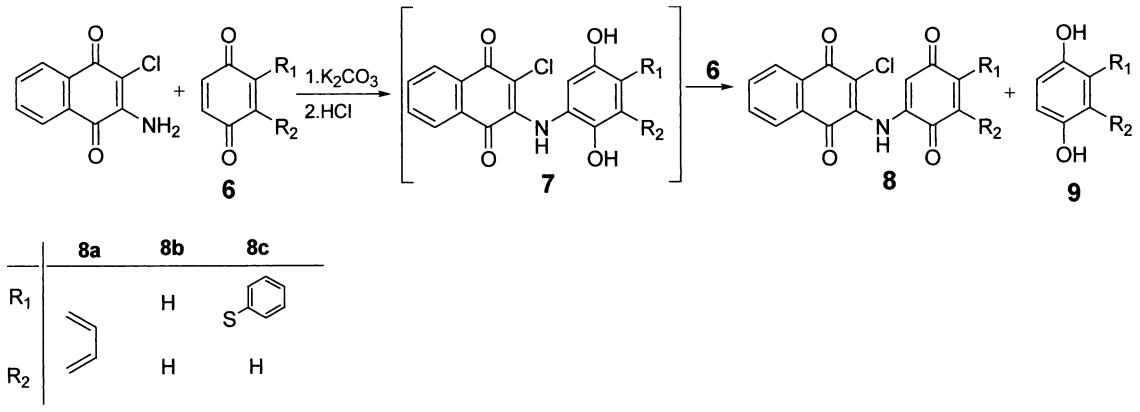
While aminoquinone **4** did not undergo a Michael-type addition with, e.g. methyl vinyl ketone, it did add to the quinonic systems **6a**–**c** yielding the nonsymmetrical diquinonylamines **8a**–**c** (Scheme 4). The accompaning products were the hydroquinones **9a**–**c**, which implies that a classical 1,4-reductive addition reaction of the amine to the quinone took place, yielding the internal quinhydrons **7a**–**c**. A redox process follows in which the intermediate **7** is oxidized by a second equivalent of the starting quinone. The yields in these reactions are lower than with the haloquinones, and the reaction mixture contains several side products originating, supposedly, from the radical producing quinhydron intermediate **7**.

This new type of bis-(quinonyl)amines are vinylogous imides and thus must have acidic character. Indeed, they undergo rapid deprotonation in slightly basic solutions (e.g. sodium bicarbonate or ammonium hydroxide) which

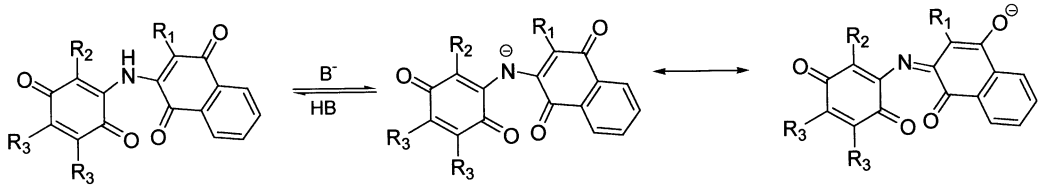


	R	R_1	R_2	R_3
5a	H	Cl	Cl	
5b	H	Br	Br	
5c	CH_3	Cl	Cl	
5d	H	Cl	Cl	Cl

Scheme 3.



Scheme 4.



Scheme 5.

is followed by a dramatic change of color. The yellow, orange or red color of the protonic form, changes to a deep blue color of the resonance-stabilized anionic form (Scheme 5). It is interesting to note that in polar solvents like DMF, DMSO, or protic solvents like alcohols, the anionic forms are free-solvated and the blue color appears without the need of a base. The optical properties of this new type of bis-(quinonyl)amines, with emphasis on their radical anion form, are now under extensive study.

2.2. Spectroscopic characterization

The ^{1}H NMR spectra ($CDCl_3$) of the symmetrical molecules **5a**–**c** exhibits two four spin systems characteristic of two different *ortho* disubstituted aromatic compounds. The four hydrogens H(C9), H(C6) and H(C19), H(C16) (Fig. 1) show chemical shifts at 8.12–8.21 and 7.95–8.05 ppm, respectively, and appear as two double doublets with J values of 7.25–7.85 and 1.32–2.10 Hz. The four protons H(C8), H(C17) and H(C7), H(C18) show chemical shifts at 7.66–7.76 and 7.70–7.81, respectively, which appear as two double triplets resulting of two overlapping *ortho* as well as *meta* splittings. The nonsymmetrical bis-(quinonyl)amine **5d** shows similar shifts and splitting patterns, but integration corresponds to one naphthalenic system only. The non-symmetrical molecule **8a** exhibits two sets of naphtho-quinonic hydrogens. The four protons H(C16), H(C19), H(C9), and H(C6) (Fig. 2) appear as four double doublets at 8.12–8.31 ppm with J values of 7.19–7.60 and 1.31–2.59 Hz. Protons H(C17) and H(C6) appear as doublets of triplets at 7.74 and 7.83 ppm, respectively. The double triplets corresponding to H(C18) and H(C8), partly overlap and form a nine peak multiplet at 7.80 ppm. The single quinonic proton appears as a singlet at 5.88 ppm. The naphthalenic protons of diquinonylamine **8b** gave a similar pattern to that of **5a**–**d** (Fig. 3) and the characteristic shifts and multiplicity of mono-substituted benzoquinone. Therefore, H(C13) apears at 5.67 ppm as a doublet (J=2.32 Hz), H(C15) apears at 6.77 ppm as a double doublet (J=10.10,

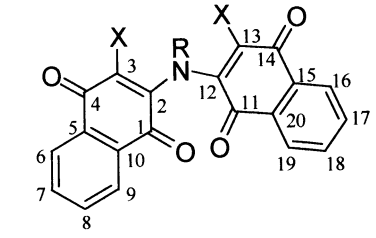


Figure 1.

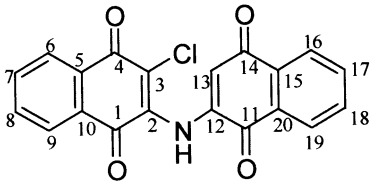


Figure 2.

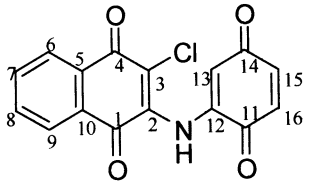


Figure 3.

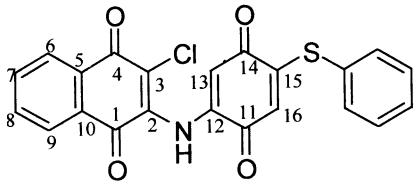


Figure 4.

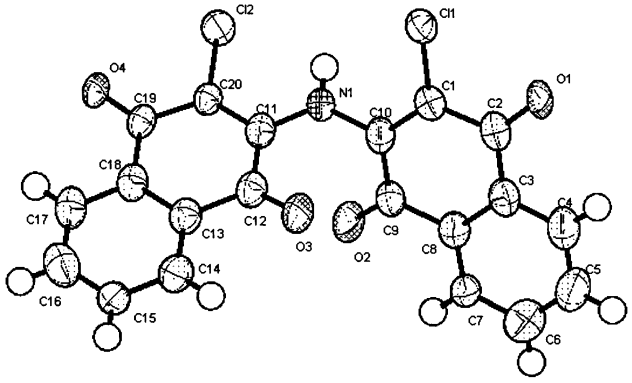


Figure 5. Molecular structure of **5a**.

2.32 Hz), and H(C13) resonate at 6.83 ppm as a doublet (J=10.10 Hz). The *S*-phenyl derivative **8c** (Fig. 4) showed two quinonic singlets at 5.67 and 6.95 ppm, and a multiplet of the aromatic ring at 7.53 ppm. In the products **5a**, **5b**, **5d**, and **8a**–**c**, a broad signal between 6.83–8.31 ppm, which disappears on treatment with D_2O is attributed to the NH protons.

All the symmetrical molecules **5a**–**c** displayed 10 signals in their ^{13}C NMR spectra. The non-symmetrical compounds **5d** and **8b** showed 16 signals, **8a** 20 and **8c** 22 peaks. The quinonic carbonyls appeared at 170–183 ppm, the carbons attached to halogens at 139–149 ppm and those attached to nitrogen at 112–135 ppm. The rest naphthalenic carbons appeared at 115–133 ppm and the quinonic carbon (in **8a**–**c**) at 109–111 ppm. The *N*-methyl of **5c** appeared at 42 ppm.

The infrared spectra of all bis-(quinonyl)amines **5a**–**d** and **8a**–**c** exhibit strong carbonylic absorption between 1651 and 1683 cm^{-1}. The N–H stretching vibrations appear between 3283 and 3318 cm^{-1}.

In the mass spectrum of compounds **5b**, **5c** and **8a**–**c**, a strong molecular ion at M^+ or $[M+H]^+$ were recorded. Compound **5d** showed the molecular ion at $[M+2H]^+$, **5a** at both $[M+3H]^+$ and $[M+5H]^+$. These two peaks in the spectrum of **5a** correspond to protonation of either one or two quinonic moieties and protonation of the amino group. Most compounds showed a strong peak corresponding to a loss of halogen atom from the molecular ion. The chloranil derivative **5d** showed a strong peak at *m*/*z* 352 originating from both dechlorination and decarbonylation. **8b** showed a parent peak at *m*/*z* 207 corresponding to 2-amino-3-chloro-1,4-naphthoquinone and **8c** displayed two fragments, at *m*/*z* 109 and at *m*/*z* 218 related to thiophenol and its dimer.

2.3. X-Ray diffraction

Fig. 5 shows the molecular structure of the di-naphthoquinonylamine **5a**. It can be seen, that the molecule has no symmetry and belongs to the *P*-1 space group. The calculated results show that each of the naphthoquinone rings system adopts a planar conformation. Thus mean deviation from plane C(1)–C(10) is equal to 0.0344 Å and the mean deviation from plane C(11)–C(20) is equal to 0.0228 Å. The value of the angle between the planes of the two rings is 55.3°. While in general the structure is similar to that of

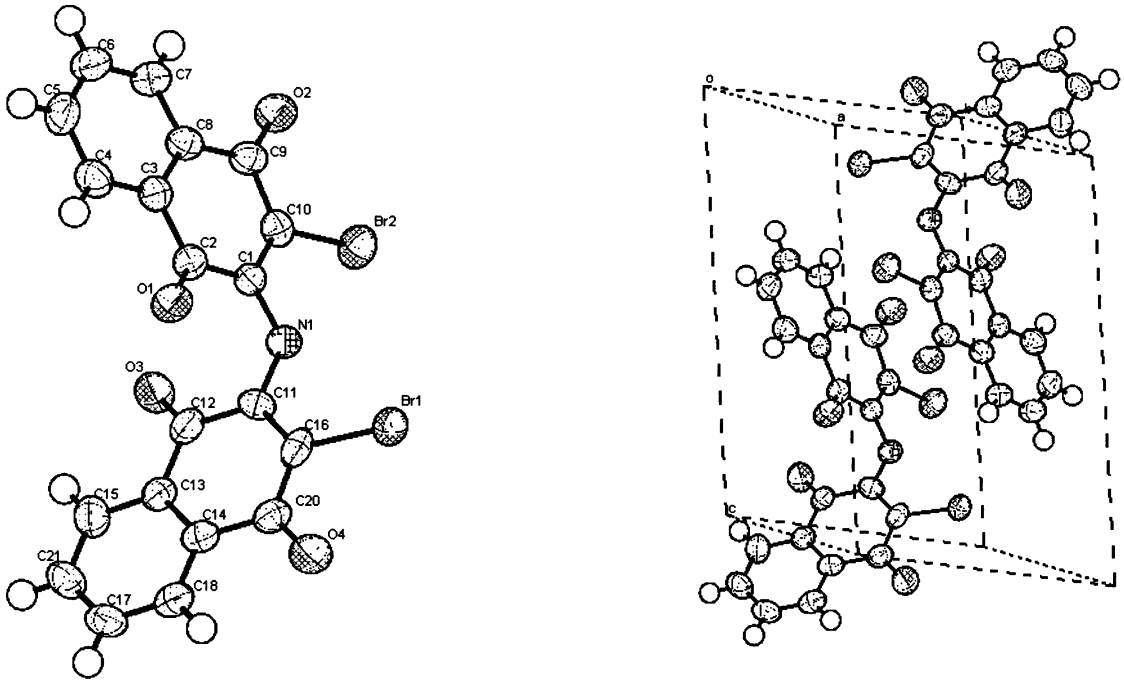


Figure 6. Molecular structure and lattice pack of **5b**.

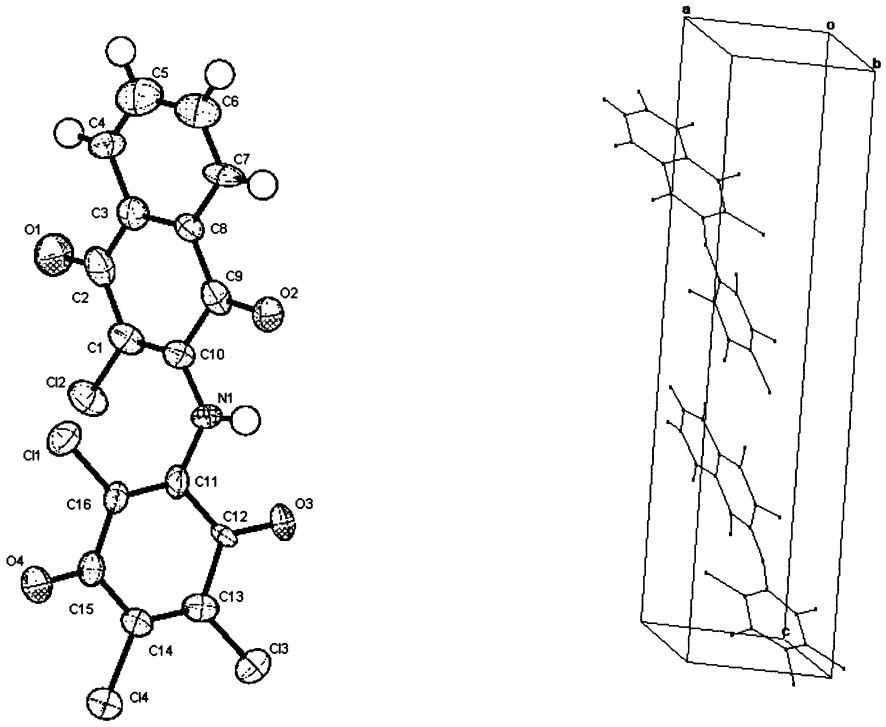


Figure 7. Molecular structure and lattice of **5d**.

other substituted naphthoquinones, several features that arise from the imidic nature of the NH and from the influence of the two chlorine atoms, are worth mentioning. The average bond distances of three carbonyl groups (1.221 Å) differ significantly from the short fourth carbonyl group (1.209 Å). The C(1)–C(10) and C(11)–C(20) distances (1.351 and 1.358 Å, respectively) are larger than the respective bonds in unsubstituted naphthoquinone (1.31 Å). This reflects the resonance structure of **5a** and the charge distribution from N(1) to the oxygens O(1) and O(4). The character of this charge distribution is also reflected by the longer aromatic bonds (1.392 Å) in the vicinity of the chlorine atom (C(3)–C(4) and C(17)–C(18)) as compared to the shorter aromatic bonds (1.378 Å) farther from the chlorine atom (C(7)–C(8) and C(13)–C(14). The peripheral aromatic bonds C(5)–C(6) and C(15)–C(16) are shorter as against the similar bonds in unsubstituted naphthoquinone (1.378 and 1.401 Å, respectively). While in usual amino-quinones a strong intramolecular hydrogen bond exist between the N–H and the quinonic carbonyl, such a bond is not possible in the present case because of the non-planarity of the system. The ring angles of the carbonyl groups (e.g. C(1)–C(2)–C(3)) is around 117.3° as compared with an angle of 121–123° in unsubstituted naphthoquinone. A very similar structure was obtained for the dibromo analog **5b** as shown in Fig. 6. Substituting the chlorine atoms with the bulkier bromine atoms, did not affect the conformation and the mode of the lattice pack. Even the angle between the two aromatic planes is 55.7°, very close to that of **5a**. The arrangement of the lattice (Fig. 6), suggests stabilizing charge-transfer interactions between the benzene moiety of one molecule with the quinonic moiety of a second molecule.

Fig. 7 represents the molecular structure of the non-symmetrical molecule **5d** composed of chloro-naphthoquinone and trichloro-benzoquinone attached to the NH group. Both quinones keep their planar configuration and the angle between them is 60.2°. As above, the arrangement in the lattice shows interaction between the trichloroquinone of one molecule and the benzenoidic moiety of a second molecule.

3. Experimental

3.1. General

All chemicals, solvents and reagents are of commercial quality and were used as received. 2-Amino-3-chloro-1,4-naphthoquinone[21] and 2-methylamino-3-chloro-1,4-naphthoquinone[22] were prepared. Column chromatography was performed on silica gel 60 (Merck). Thin layer chromatography was carried out on Merck 5554 pre-coated silica gel 60 F_{254} aluminum sheets. IR spectra (KBr discs) were recorded on a Nicolet 5 ZDX FT-spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained on Bruker DMX 500 instrument. Chemical shifts for NMR were determined relative to the internal standard tetramethylsilane (δ 0.00), $CHCl_3$ (δ 7.26) for ^{1}H spectra, and $CDCl_3$ (δ 77.0) for ^{13}C spectra. All ^{1}H NMR data listed have the following order: chemical shift (ppm), multiplicity, number of protons, coupling constant (Hz). The ^{13}C NMR data listed have the following order: chemical shift (ppm), assignment. Mass spectra (CI in isobutane) were obtained using a Finnigan 4020 quadropole mass spectrometer. Elemental analyses were obtained from the microanalytical laboratory of the Hebrew University, Jerusalem. Melting points were determined using a Thomas–Hoover capillary apparatus and are uncorrected. X-Ray intensity data were measured on a

standard Bruker SMART 6K CCD diffractometer [l(MoKa)=0.711069 Å, graphite monochromator, a scan width of 0.3° and exposure time of 10 s/frame, detector-crystal distance 4.95 cm]. Data were corrected for absorption using SADABS program. The structures were solved by direct methods and refined by least squares in full-matrix approximation. Hydrogen atoms were placed to the calculated positions and were refined using the 'riding model'. SHELXTL [Bruker AXS, 1998] software package were used for calculations and drawings. The angles between planes and lattice packs were calculated using Oscail Version 8 software. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers 161188-161190. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-01223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

3.2. General procedure for the synthesis of 5a–d

Haloquinone (12.0 mmol) and aminoquinone (10 mmol) were added to a solution of approximately 1 g of potassium carbonate in DMF (50 mL, pH=12) and the mixture was allowed to stir for 2 h at room temperature. Addition of HCl (2% ice-water solution, 100 mL) caused precipitation of the crude product. This was filtered off, dissolved in CH_2Cl_2 and purified by silica gel column chromatography with methylene chloride as eluant. The products were recrystallized from glacial acetic acid to yield orange to red fine crystals. It is interesting to note that a typical feature of compounds **5a**, **5b**, and **5d** is their color changes to strong blue upon exposure to ammonia vapors.

3.2.1. *N,N*-Bis(3-chloro-1,4-naphthoquinonyl)amine (5a). (2.3 g, 58%) was obtained from 2,3-dichloro-1,4-naphthoquinone (2.72 g) and 2-amino-3-chloro-1,4-naphthoquinone (2.07 g) as bright orange needles melting at 273–274°C, (Found: C, 60.04; H, 2.28; Cl, 17.50, N, 3.39 $C_{20}H_9Cl_2NO_4$ requires C, 60.33; H, 2.28; Cl, 17.81; N, 3.52%); ν_{max} (KBr) 3318, 1676, 1660 cm^{-1}; δ_H (500 MHz) 7.08 (brs, 1H), 7.76 (dt, 2H, J=7.5, 1.8 Hz), 7.81 (dt, 2H, J=7.5, 1.5 Hz), 8.05 (dd, 2H, J=7.2, 1.8 Hz), 8.21 (dd, 2H, J=7.2, 1.8 Hz). δ_C (125 MHz) (numbering of the carbons according to the X-ray diagram of **5a**, Fig. 5) 125.0 (C-6 and C-15), 127.2 (C-5 and C-16), 127.4 (C-7 and C-14), 130.6 (C-4 and C-17), 131.5 (C-8 and C-13), 133.9 (C-3 and C-18), 134.8 (C-10 and C-11), 142.4 (C-1 and C-20), 176.9 (C-9 and C-12), 178.8 (C-2 and C-20). m/z 403 (M^++5, 100), 401 (M^++3, 74), 364 (M^+−Cl, 66).

3.2.2. *N,N*-Bis(3-bromo-1,4-naphthoquinonyl)amine (5b). (3.5 g, 69%) was obtained from 2,3-dibromo-1,4-naphthoquinone (3.7 g) and 2-amino-3-bromo-1,4-naphthoquinone (2.52 g) as bright orange needles melting at 240–242°C. ν_{max} (KBr) 3300, 1673 cm^{-1}; δ_H (500 MHz) 7.00 (brs, 1H), 7.67 (dt, 2H, J=7.5, 1.3 Hz), 7.72 (dt, 2H, J=7.6, 1.4 Hz), 7.95 (dd, 2H, J=7.5, 1.3 Hz), 8.16 (dd, 2H, J=7.8, 2.0 Hz). δ_C (125 MHz), (numbering of carbons according to the X-ray diagram of **5b**, Fig. 6) 119.0 (C-5 and C-19), 127.1 (C-6 and C-17), 127.4 (C-4 and C-15), 130.7 (C-7 and C-18), 131.5 (C-3 and C-13), 133.9 (C-8 and C-14), 134.8 (C-1 and C-11), 145.5 (C-10 and C-16), 177.0 (C-2 and C-12), 178.3 (C-9 and C-20). m/z 488 (MH^+, 100), 406 (M^+−Br, 66).

3.2.3. *N*-Methyl-*N,N*-bis (3-chloro-1,4-naphthoquinonyl)-amine (5c). (2.5 g, 61%) was obtained from 2,3-dichloro-1,4-naphthoquinone (2.72 g) and 2-methylamino-3-chloro-1,4-naphthoquinone (2.22 g). The product was obtained as red needles and melted at 229–231°C. ν_{max}(KBr) 2960, 1666, 1651 cm^{-1}; δ_H (500 MHz) 3.58 (s, 1H), 7.66 (dt, 2H, J=7.4, 1.3 Hz), 7.70 (dt, 2H, J=7.5, 1.3 Hz), 8.05 (dd, 2H, J=7.8, 2.1 Hz), 8.12 (dd, 2H, J=7.5, 1.5 Hz); δ_C (125 MHz) (according to X-ray diagram of **5a**, Fig. 5) 41.6 (CH_3), 127.1 (C-6 and C-15), 127.4 (C-5 and C-16), 130.7 (C-7 and C-14), 131.3 (C-4 and C-17), 131.4 (C-8 and C-13), 133.9 (C-3 and C-18), 134.4 (C-10 and C-11), 148.8 (C-1 and C-20), 176.0 (C-9 and C-12), 179.8 (C-2 and C-20). HRMS (CI/i-bu) (m/z): 411.002176 (MH^+, calcd. 411.006513 for $C_{21}H_{11}Cl_2NO_4$), 376 (M^+−Cl).

3.2.4. *N*-(3,5,6-trichloro-1,4-benzoquinon-2-yl)-*N*-(3-chloro-1,4-naphthoquinonyl)amine (5d). (3.3 g, 79%) was obtained from chloranil (2.95 g) and 2-amino-3-chloro-1,4-naphthoquinone (2.07 g) as dark red needles melting at 231–232°C. (Found: C, 46.01; H, 1.24; Cl, 33.89, N, 3.42. $C_{16}H_5Cl_4NO_4$ required C, 46.08; H, 1.21; Cl, 34.01; N, 3.36%); ν_{max}(KBr) 3277, 1683, 1673, 1665 cm^{-1}; δ_H (500 MHz) 6.83 (brs, 1H), 7.70 (dt, 1H, J=7.5, 1.2 Hz), 7.75 (dt, 1H, J=7.5, 1.2 Hz), 7.98 (dd, 1H, J=7.5, 1.3 Hz), 8.13 (dd, 1H, J=7.6, 1.3 Hz), δ_C (125 MHz) (according to the X-ray diagram of **5d**, Fig. 7) 121.2 (C-6), 126.2 (C-5), 127.3 (C-7), 127.6 (C-4), 130.3 (C-8), 131.3 (C-3), 134.5 (C-10), 135.2 (C-11), 138.6 (C-1), 140.8 (C-16), 141.5 (C-13), 148.9 (C-14), 170.3 (C-9), 172.4 (C-2), 176.7 (C-12), 178.6 (C-15). m/z 417 (M^+), 380 (M^+−Cl, 100), 352 (M^+−Cl–CO).

3.3. General procedure for the synthesis of 8a–c

The quinone (20.0 mmol) and 2-amino-3-chloro-1,4-naphthoquinone (2.08 g, 10 mmol) were added to a solution of approximately 1 g of potassium carbonate in DMF (50 mL, pH=12) and the mixture was allowed to stir for 12 h at room temperature. Addition of HCl (2% ice-water solution, 100 mL) caused precipitation of the crude product. It was filtered off and purified by silica gel column chromatography with methylene chloride as eluant. The products were recrystallized from glacial acetic acid. A change of color to strong blue was observed upon exposure to ammonia vapors.

3.3.1. *N*-(Naphthoquinonyl)-*N*-(3-chloro-1,4-naphthoquinonyl)amine (8a). This compound was prepared from 1,4-naphthoquinone (3.16 g) and obtained as yellow needles (1.49 g, 41%) melting at 246–248°C. (ν_{max}(KBr) 3304, 1681, 1662 cm^{-1}; δ_H (500 MHz) 5.88 (s, 1H), 7.74 (dt, 1H, J=7.5, 1.3 Hz), 7.80 (m, 2H), 7.83 (td, 1H, J=7.4, 1.5 Hz), 8.12 (dd, 1H, J=7.6, 1.3 Hz), 8.16 (dd, 1H, J=7.2, 2.3 Hz), 8.18 (dd, 1H, J=7.3, 2.6 Hz), 8.23 (dd, 1H, J=7.5, 1.5 Hz), 8.31 (brs, 1H). δ_C (125 MHz) (according to Fig. 2) 110.4 (C-13), 115.3 (C-12), 126.5 (C-2), 126.8 (C-17), 127.2(C-18), 127.4 (C-8), 127.6

(C-7), 130.2 (C-16), 130.4 (C-19), 131.7 (C-9), 132.5 (C-6), 133.2 (C-15), 134.2 (C-20), 135.0 (C-10), 135.2 (C-5), 139.8 (C-3), 177.2 (C-14), 179.6 (C-11), 180.8 (C-1), 183.5 (C-4). HRMS (CI/i-bu) (*m/z*): 363.026711 (M^+, calcd. 363.029836 for $C_{20}H_{10}ClNO_4$), 319 ($M^+-C_2H_4O$).

3.3.2. *N*-(1,4-Benzoquinonyl)-*N*-(3-chloro-1,4-naphthoquinonyl)amine (8b). (0.85 g, 27%) was prepared from 1,4-benzoquinone (2.16 g) and obtained as yellow needles melting at 217–218°C. ν_{max}(KBr) 3288, 1678, 1662 cm^{-1}; δ_H (500 MHz), 5.67 (d, 1H, *J*=2.3 Hz), 6.77 (dd, 1H, *J*=10.1, 2.3 Hz), 6.83 (d, 1H, *J*=10.1 Hz), 7.79 (dt, 1H, *J*=7.5, 1.5 Hz), 7.82 (td, 1H, *J*=7.1, 1.5 Hz), 8.00 (brs., 1H), 8.17 (dd, 1H, *J*=7.9, 1.3 Hz), 8.22 (dd, 1H, *J*=7.3, 1.6 Hz). δ_C (125 MHz) (according to Fig. 3) 109.8 (C-15), 110.7 (C-16), 112.5 (C-13), 117.6 (C-12), 126.2(C-2), 127.1 (C-8), 127.3 (C-7) 127.4 (C-9), 127.9 (C-6), 132.3 (C-10), 135.7 (C-5), 147.7 (C-3), 176.5 (C-14), 179.2 (C-11), 181.6 (C-1), 185.8 (C-4). HRMS (CI/i-bu) (*m/z*): 314.024323 (MH^+, calcd. 314.022011 for $C_{16}H_9ClNO_4$), 280 (M^++ 2H–Cl), 207 (2-amino-3-chloro-1,4-naphthoquinone), 110 (hydroquinone).

3.3.3. *N*-(5-Phenylthio-benzoquinonyl)-*N*-(3-chloro-1,4-naphthoquinonyl)amine (8c). (1.01 g, 24%) was prepared from *S*-phenylthiobenzoquinone (4.32 g) and obtained as red needles melting at 261–262°C. ν_{max}(KBr) 3283, 3055, 1678, 1652, 1555 cm^{-1}; δ_H (500 MHz) 5.67 (s, 1H), 6.95 (s, 1H), 7.53 (m, 5H), 7.67 (t, 1H, *J*=7.5 Hz), 7.75 (t, 1H, *J*=7.6 Hz), 7.82 (d, 1H, *J*=7.6 Hz), 7.86 (brs., 1H), 8.16 (d, 1H, *J*=7.7 Hz).δ_C (125 MHz) (according to Fig. 4) 110.3 (C-13), 110.7 (C-16), 116.1 (C-15), 117.2 (C-12), 126.8(C-2), 127.1 (C-8), 127.3 (C-7), 127.5 (C-9), 128.0 (C-6), 128.6, 128.7, 129.3, 130.3, 130.5 (5C of S-Ph), 134.3 (C-10), 135.4 (C-5), 135.7 (C-S), 137.0 (C-3),178.0 (C-11), 179.8 (C-1), 182.0 (C-14), 183.2 (C-4). HRMS (CI/i-bu) (*m/z*): 422.023797 (MH^+, calcd. 422.025383 for $C_{22}H_{13}ClNO_4S$), 218 ($C_{12}H_{10}S_2$), 109 (C_6H_5S).

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