# DDQ-promoted thiocyanation of aromatic and heteroaromatic compounds

**Hamid R. Memarian, Iraj Mohammadpoor-Baltork, and Kobra Nikoofar**

**Abstract:** Thiocyanation of various aromatic and heteroaromatic compounds has been achieved using ammonium thiocyanate in the presence of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in methanol solution at room temperature and under reflux condition. The rate of reaction is influenced by the electron-donor ability of the aromatic nucleus.

*Key words:* amines, DDQ, indoles, thiocyanation.

**Résumé :** On a effectué la thiocyanatation de divers composés aromatiques et hétéroaromatiques en utilisant du thiocyanate d'ammonium en présence de 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), en solution dans le méthanol, à la température ambiante ainsi que sous des conditions de reflux du méthanol. La vitesse de la réaction est influencée par le caractère électrodonneur des substituants sur le noyau aromatique.

*Mots-clés :* amines, DDQ, indoles, thiocyanatation.

[Traduit par la Rédaction]

## Introduction

The electrophilic thiocyanation of aromatic and heteroaromatic compounds is an important process of carbon–sulfur bond formation in organic synthesis, since the nucleophilic attack of the thiocyanate ion to the aromatic nucleus by displacement reactions is not the easy way to form thiocyanated compounds. Thiocyanates constitute an interesting group, which could be readily transformed into other sulfur-bearing functionalities (1–4), especially for producing drugs and pharmaceuticals (5). Therefore, it is important to find new methods for the thiocyanation of aromatic systems. Several methods have been developed for the thiocyanation of aromatic systems using bromine/potassium thiocyanate (6), *N*-thiocyanatosuccinimide (7), cerric ammonium nitrate (CAN) (8), montmorillonite K-10 (9), iodine/methanol (4), oxone (10), and ferric(III) chloride (11). However, some of these methods suffer from disadvantages, such as low yields, especially in the case of aromatic amines, the use of strongly acidic or oxidizing conditions, the use of special conditions (long reaction time and (or) high temperature), and also the use of expensive reagents. In this research, we have developed a new route for the thiocyanation of aromatic and heteroaromatic systems.

2,3-Dichloro-5,6-dicyanobenzoquinone (DDQ) is a versatile reagent for organic synthesis. Owing to its oxidizing ability and also its relative stability under various reaction conditions, this reagent has been used for various organic transformations, e.g., benzylic oxidation of Catechine (12), oxidation of benzhydrols (13), selective oxidation of allylic or benzylic hydroxyl groups (14), anodic oxidation of naphthalenes (15), and oxidation of thioglycosides (16).

DDQ has also been used alone for a wide range of transformations, such as dehydrogenation (17), carbon–carbon bond cleavage (18), and alcoholysis of epoxides (19); or in combination with triphenylphosphine for the conversion of epoxides to halohydrines (20), thiocyanation of α-hydroxy phosphonates (21), and thiocyanation and isothiocyanation of some alcohols and ethers (22). DDQ is also a well-known electron-acceptor species, and its interaction with a variety of electron donors has been the subject of several investigations concerning the formation of charge-transfer (CT) complexes (23–28). Herein, we wish to report an effective and benign method for the thiocyanation of aromatic and heteroaromatic compounds using ammonium thiocayanate, as a thiocyanating agent, in the presence of DDQ at room temperature (Method A) and under reflux conditions (Method B).

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## Results and discussion

### Solvent effect and optimization of the reactants

Since the nature of solvent influences the rate of reaction, thiocyanation of 2-methylindole as a model substrate was performed in various solvents at room temperature. According to the data presented in Table 1, methanol has been chosen as the best solvent for this purpose. One reason for the observed different reaction times could be the solubility of the starting materials, especially DDQ, in solvents used in this study. Therefore, we carried out the reaction with the same concentration of the dissolved reactants in *n*-hexane (as non-polar solvent) and methanol (as polar solvent). We found that methanol is the suitable solvent for our reaction.

The next step is the optimization of $NH_4SCN$:DDQ molar ratio in thiocyanation reaction under two reaction conditions.

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**Table1.** Solvent effect on the reaction of 2-methylindole with $NH_4SCN$ in the presence of DDQ at room temperature (method A).

| Entry | Solvent | Time (min) | Yield (%) |
|---|---|---|---|
| 1 | $H_2O$ | 180 | 0 |
| 2 | $H_2O$–$CH_3OH$ (1:1) | 70 | 10 |
| 3 | DMF | 75 | 10 |
| 4 | $CH_3CN$ | 25 | 99 |
| 5 | $CH_2Cl_2$ | 90 | 85 |
| 6 | $CHCl_3$ | 90 | 75 |
| 7 | *n*-hexane | 180 | 40 |
| 8 | EtOAc | 40 | 93 |
| 9 | $CH_3OH$ | 15 | 99 |

**Note:** All reactions were performed in the presence of 2 mmol of $NH_4SCN$ and 1.5 mmol of DDQ in 5 mL of solvent.

**Table 2.** Optimization of $NH_4SCN$:DDQ molar ratio in the thiocyanation of 2-methylindole under two different conditions.

| Entry | Molar ratio of $NH_4SCN$:DDQ | Method A[a] Time (min) [yield (%)] | Method B[b] Time (min) [yield (%)] |
|---|---|---|---|
| 1 | 3:1.5 | 15 [99] | 15 [99] |
| 2 | 3:0.5 | — | 90 [35] |
| 3 | 3:1 | 40 [75] | 70 [85] |
| 4 | 3:1.25 | 60 [88] | 15 [90] |
| 5 | 2:1.25 | 25 [95] | 15 [99] |
| 6 | 1:1.5 | — | 35 [62] |
| 7 | 2:1.5 | 15 [99] | 15 [99] |
| 8 | 2:1 | — | 40 [78] |
| 9 | 2.5:1.5 | 15 [99] | — |

**Note:** In all cases, methanol (5 mL) was used as solvent.
[a]Room temperature conditions.
[b]Under reflux conditions.

The results presented in Table 2 showed that the optimized molar ratio of $NH_4SCN$:DDQ is 2:1.5 for method A and 2:1.25 for method B. These data also show that an increase of the amount of $NH_4SCN$ did not affect the yield or the rate of the reaction.

**Thiocyanation of aromatic and heteroaromatic systems**

Under optimized reaction conditions, the thiocyanation of different aromatic and heteroaromatic compounds was investigated under two conditions, at room temperature (method A) and under reflux conditions (method B). The results are summarized in Table 3. Clearly, various compounds were converted to their corresponding thiocyanation products in good to excellent yields. The products were identified by IR, $^1H$ NMR, and MS spectra. IR spectra showed the characteristic peaks of –SCN between 2120–2150 $cm^{-1}$ and the C–S stretching between 650–750 $cm^{-1}$. The regiochemistry of substitution was achieved by the interpretation of $^1H$ NMR spectra and their comparison with the spectra and physical data of authentic samples (see Experimental Section).

According to the results obtained from the control experiment and the results presented in Table 3, we can summarize the following:

(*i*) The presence of DDQ is necessary for the reaction because the reaction of **1b** as a test compound with $NH_4SCN$ in methanol in the absence of DDQ did not proceed at all.

(*ii*) The use of DDQ in a molar ratio of 1.25 and 1.5 to 1 of the aromatic compound indicates that DDQ does not act as a catalyst, since it is consumed during the reaction.

(*iii*) The times and the yields of the reactions are dependent on the electron-donating ability of the aromatic and heteroaromatic compounds.

On the basis of the forgoing results, the following mechanism is proposed for the reaction, by taking (**1a**) as an example (Scheme 1).

According to the proposed mechanism, either the formation of a π complex between the aromatic system and DDQ can occur (path a) or an electron-transfer process leads to the formation of an ion pair, namely, the radical cation of aromatic system and $DDQ^{\bullet-}$ (path b). Nucleophilic attack of one of these intermediates by the thiocyanate ion leads to the formation of a thiocyanated radical system accompanied by $DDQ^{\bullet-}$. An electron transfer from the radical intermediate to $DDQ^{\bullet-}$, followed by the proton abstraction, accomplished the reaction under the formation of the thiocyanated product and $DDQH^-NH_4^+$. The following experiments support the involvement of a π complex (path a) in the reaction rather than the electron-transfer process (path b):

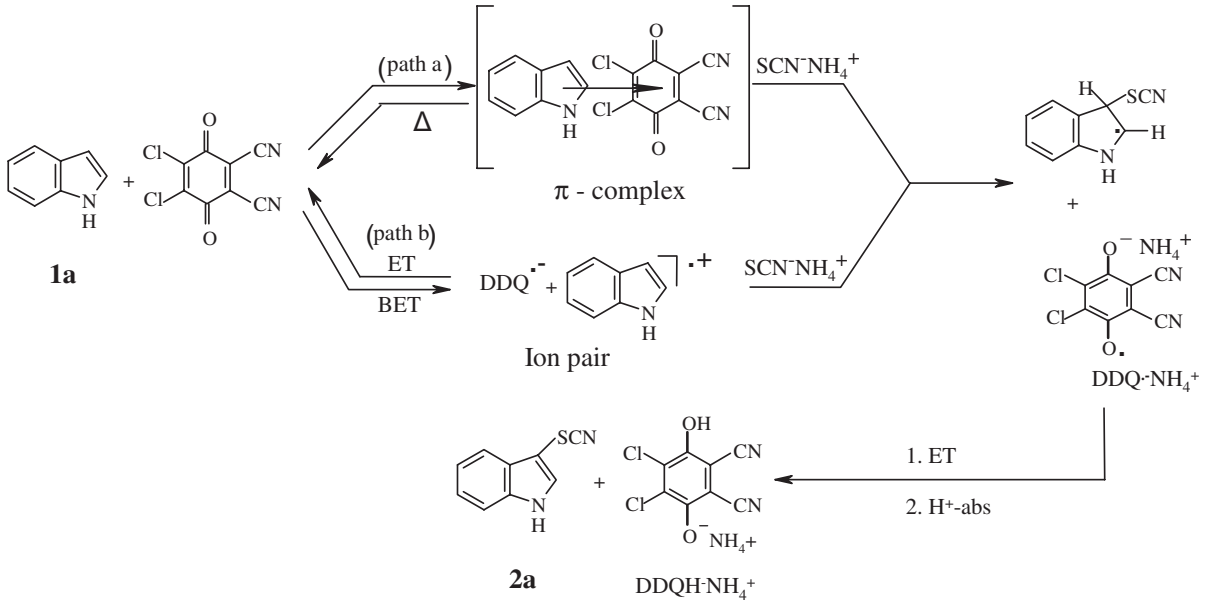
(*i*) The electronic absorption spectra of 0.001 mol/L solutions of the donor molecule **1b** or **1c** with the acceptor molecule DDQ (0.001 mol/L) and also the mixture of either **1b** + DDQ or **1c** + DDQ in methanol show the formation of the weak charge-transfer (CT) complexes between both donor and acceptor molecules (Figs. 1 and 2).

(*ii*) Addition of ammonium thiocyanate to the mixture of either **1b** + DDQ or **1c** + DDQ at room temperature causes a decrease of CT-complex absorption (Figs. 3 and 4).

(*iii*) To obtain more information about the formation of charge-transfer complexes between DDQ and the aromatic and heteroaromatic systems as a key step in the reaction, conductance measurements, as a much sensitive method, was used. Conductance measurements were carried out on the solutions of **1b**, **1c**, DDQ and their mixtures **1b** + DDQ and **1c** + DDQ at three molar ratios (0.5:1, 1:1, and 2:1) at 23 °C and 50 °C. The results are summarized in Table 4.

The results showed that the addition of DDQ to the solutions of **1b** and **1c** causes a sharp increase in the conductivity. The conductivities of the mixture of **1b** with DDQ or **1c** with DDQ are more than the sum of conductivities of the separated compounds. The results clearly indicate that the charge-transfer complexes are more mobile than the individual compounds (29). The differences between the conductivities of the mixture of **1b** with DDQ and (**1c**) with DDQ and the sum of the conductivities of the individual compounds at the same concentration could be related to the extent of CT formation, which is directly related to the electron-donor ability of **1b** compared with **1c**. This is supported by comparing the rate of thiocyanation of **1b** (15 min) with **1c** (30 min). These experiments show clearly that by increasing DDQ ratio from 0.5 to 1 and 2, the difference in conductivity is increased, but there is no difference between the conductivities of the 1:1 and 1:2 molar ratios. This result

**Scheme 1.**



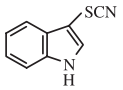
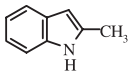
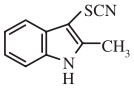
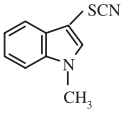
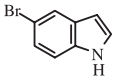
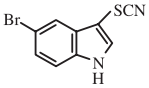
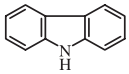
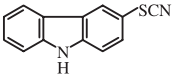
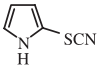
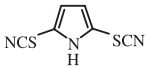
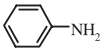
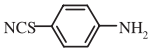
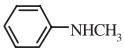
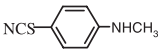
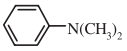
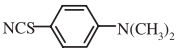
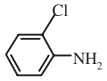
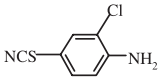
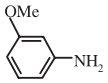
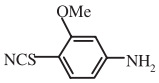
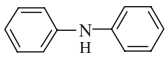
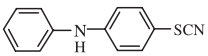
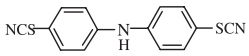

confirms that a 1:1 complex is formed between the donor and the acceptor molecules (Figs. 5 and 6).

Interestigly, conductivity measurements showed that by increasing the temperature, the conductivities are decreased. This clearly indicates that the cleavage of a π complex occurs by increasing the temperature and supports the reaction path a. In path b and formation of the ionic intermediates, we expected that ion mobility should be increased by increasing temperature. All these observations support the involvement of a π complex in the thiocyanation in our study. These observations are also supported by the fact that the reaction of thiophene, furan, pyridine, and their benzocondenced derivatives, namely, benzothiophene, benzofuran, and quinoline, as less electron-donor compounds compared with the compounds considered in this study, under the same reaction conditions did not result in changing the color of solution (indicating the lack of any CT-complex formation) or in the formation of any product(s) even after stirring the reaction mixture at room temperature for 6 h.

The results presented in Table 3 showed that various aromatic and heteroaromatic compounds are converted to their corresponding thiocyanated derivatives in good to excellent yields. A comparison of the times for the maximum progression of reactions indicates that the electron-donor ability of compounds is an important factor for this reaction. These results indicate that the steric and electronic effects (e.g., the HOMO energy) are responsible for the CT-complex formation, which supports our suggestion of the involvement of the π complex in the rate-determining step. In comparison with the results obtained by the thiocyanation of indolic compounds (Table 3, entries 1–4), we found that the inductive effect of the methyl group at the 2 position (Table 3, entry 2) decreases the time required for the completion of the reaction, compared with compound **1a** (Table 3, entry 1) that does not have this substituent. Contrary to these observations, the presence of the methyl group at position 1 (compound **1c**) increases the time required for the completion of the reaction. It is expected that the presence of the methyl group in position 1, should increase the electron-donating character of the nitrogen; therefore, a reaction-time decrease should be observed for the thiocyanation of compound **1c** (Table 3, entry 3) compared with compound **1a** (Table 3, entry 1). The obtained reaction times do not confirm these suggestions. The reason is probably that because of the rehybridization of the nitrogen atom from $sp^3$ to $sp^2$ for better participation of the nitrogen lone pair in a conjugative system, the repulsive effect of the methyl group in position 1 (compound **1c**) with the hydrogen in position 7 is increased, which leads to the aversion of the nitrogen of pushing electron to the pyrrole ring to increase the HOMO energy. Due to cross conjugation of the nitrogen to both phenyl rings in carbazole **1e**, compared with indole **1a**, the energy of the HOMO should lay lower; therefore, a longer reaction time is expected. The most interesting results were obtained for the thiocyanation of aniline and its *N*- and ring substituted derivatives. While the presence of the methyl group(s) on the nitrogen decreases the reaction time, the presence of electron-withdrawing substituents, such as chlorine, methoxy, or phenyl groups, increases the reaction time. The data reported in Table 3 also showed that for pyrrole **1g** and diphenylamine **1l**, both mono- and dithiocyanated products were formed.

Concerning the regiochemistry of thiocyanate-ion addition, especially for indole and its derivatives, two possible radical intermediates **3** (a donor-substituted radical center) and **4** (a benzylic radical center) should be considered (Scheme 2). The stability of these radical intermediates explains the direction of thiocyanate addition to the heteroaromatic ring. The conjugation of a radical center in **4** with the aromatic ring should disturb the aromaticity of ring, whereas the interaction of the nitrogen lone pair with the adjacent radical center in **3** should increase the stabilization of a radical center, while the aromaticity of ring stays intact (30). For other starting materials (Table 3, entries 5–12), the

**Table 3.** Thiocyanation of aromatioc and heteroaromatic compounds with $NH_4SCN$ in the presence of DDQ under different reaction conditions.

| Entry | Substrate | | Product(s)[a] | | Method A[b] | | Method B[c] | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Time (min) | Yield[d] (%) | Time (min) | Yield[d] (%) |
| 1 |  | **1a** |  | **2a** | 20 (50)[e] | 97 (94)[e] | 20 | 99 |
| 2 |  | **1b** |  | **2b** | 15 (30) | 98 (98) | 15 | 99 |
| 3 |  | **1c** |  | **2c** | 30 (60) | 98 (97) | 30 | 97 |
| 4 |  | **1d** |  | **2d** | 25 (45) | 97 (97) | 25 | 99 |
| 5 |  | **1e** |  | **2e** | 140 (240) | 52 (45) | 70 | 50 |
| 6 |  | **1f** |  | **2fa** | 35 (45) | 63 (69) | 20 | 54 |
| | | |  | **2fb** | | 32 (25) | | 41 |
| 7 |  | **1g** |  | **2g** | 40 (60) | 95 (92) | 35 | 98 |
| 8 |  | **1h** |  | **2h** | 30 (45) | 98 (95) | 20 | 98 |
| 9 |  | **1i** |  | **2i** | 20 (35) | 98 (97) | 20 | 98 |
| 10 |  | **1j** |  | **2j** | 50 (75) | 94 (90) | 40 | 94 |
| 11 |  | **1k** |  | **2k** | 30 (40) | 96 (94) | 25 | 95 |
| 12 |  | **1l** |  | **2la** | 90 (130) | 51 (58) | 50 | 53 |
| | | |  | **2lb** | | 29 (22) | | 29 |

[a]All products were identified by compariing their physical and spectral data with those of the authentic samples (See also the Experimental Section).
[b]Room temperature, molar ratio of $NH_4SCN$:DDQ = 2:1.5.
[c]Reflux conditions, molar ratio of $NH_4SCN$:DDQ = 2:1.25.
[d]Isolated yields.
[e]The numbers in parentheses show the time and yield of the reaction in the presence of 1.25 mmol of DDQ.

**Fig. 1.** Electronic absorption spectra of **1b**–DDQ reaction in $CH_3OH$. (A) [**1b**] = 0.001 mol/L, (B) [DDQ] = 0.001 mol/L, (C) **1b**–DDQ mixture: [**1b**] = [DDQ] = 0.001 mol/L.

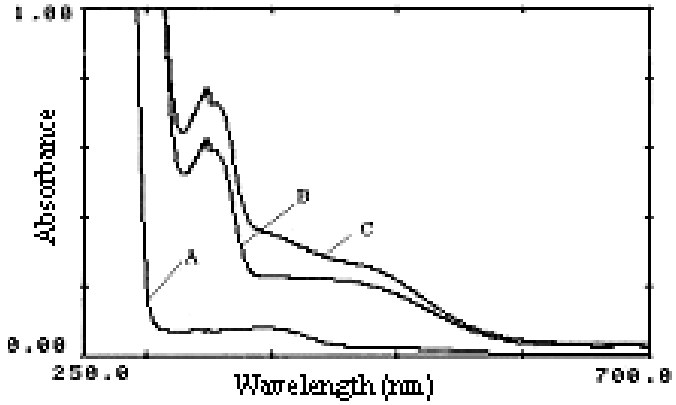



**Fig. 2.** Electronic absorption spectra of **1c**–DDQ reaction in $CH_3OH$. (A) [**1c**] = 0.001 mol/L, (B) [DDQ] = 0.001 mol/L, (C) **1c**–DDQ mixture: [**1c**] = [DDQ] = 0.001 mol/L.

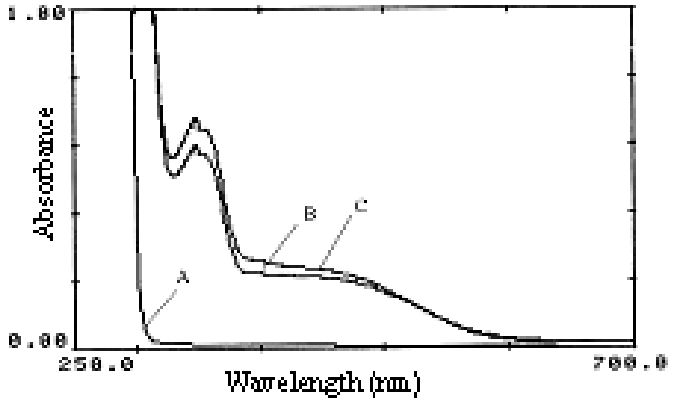



**Fig. 3.** Time evolution of the UV–vis spectra for the reaction of $NH_4SCN$ with DDQ and 2-methylindole (**1b**) CT-complex at room temperature. The spectra were taken at 2 min intervals.

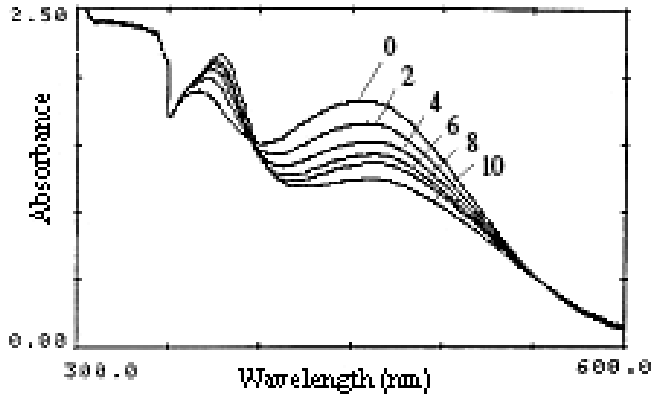
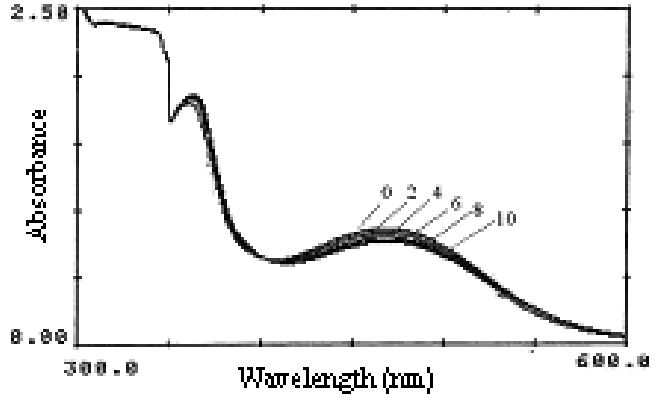



**Fig. 4.** Time evolution of the UV–vis spectra for the reaction of $NH_4SCN$ with DDQ and 1-methylindole (**1c**) CT-complex at room temperature. The spectra were taken at 2 min intervals.




resonance effect of the nitrogen lone pair directs the position of thiocyanate addition after complexation with DDQ.

## Experimental

Melting points were determined using a Stuart Scientific SMP2 capillary apparatus and are uncorrected. IR spectra were recorded from KBr discs (unless otherwise mentioned) on Shimadzu IR-435. $^1$H NMR spectra were recorded with a Brucker drx 500 (500 MHz) machine. They are reported as follows: chemical shifts (multiplicity, number of protons, coupling constants *J* (Hz), and assignment). Mass spectra were obtained on Platform II spectrometer from Micromass; EI mode at 70 eV. Elemental analysis was run on CHN-O-RAPID analyzer from Heraeus. Conductance measurements were carried out with an ORION (**1c**) Model 180 coductivity meter. A dip-type cell with a cell constant of 0.723 $cm^{-1}$ of platinum blank was used. Stock solutions of **1b** and DDQ were prepared in methanol. Varying concentrations of DDQ were added to a fixed concentration of **1b** and **1c** to prepare the desired DDQ to **1b** or **1c** molar ratios of 0.5:1, 1:1, and 2:1 for conductance measurements at 23 and 50 °C. Preparative layer chromatography (PLC) was carried out on 20 × 20 $cm^2$ plates, coated with a 1 mm layer of Merck silica gel $PF_{254}$, prepared by applying the silica gel as a slurry and dying in air.

### General procedure for the thiocyanation of aromatic and heteroaromatic compounds at room temperature (method A)

To a solution of the aromatic or heteroaromatic compound (1 mmol) and $NH_4SCN$ (2 mmol) in $CH_3OH$ (5 mL), was added DDQ (1.5 mmol) at room temperature. The reaction mixture was stirred for the appropriate time according to Table 3. The progress of the reaction was monitored by TLC. The solvent was evaporated; the residue was diluted with water (10 mL) and extracted with chloroform (3 × 10 mL). The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The resulting crude product was purified by plate chromatography on silica gel (PLC; eluent: *n*-hexane–EtOAc, 9:1). Further recrystallization from petroleum ether – EtOAc gives the pure product (Table 3).

### General procedure for the thiocyanation of aromatic and heteroaromatic compounds under reflux conditions (method B)

To a solution of the aromatic or heteroaromatic compound (1 mmol) and $NH_4SCN$ (2 mmol) in $CH_3OH$ (5 mL), was

**Table 4.** Observed conductances (μs/cm$^2$) of charge-transfer complexes **1b** and **1c** with DDQ at different molar ratios at 23 and 50 °C in methanol solution.

| Molar ratio[a] | 0:1[b] | | 0.5:1[c] | | 1:1[c] | | 2:1[c] | |
|---|---|---|---|---|---|---|---|---|
| *T* °C | 23 | 50 | 23 | 50 | 23 | 50 | 23 | 50 |
| **1b** | 0.82 | 15.35 | 48.34 | 5.85 | 81.21 | 26.05 | 90.08 | 30.65 |
| **1c** | 0.79 | 15.2 | 47.77 | 5 | 68.24 | 14.9 | 70.71 | 21.5 |

**Note:** The values refer to the corrected conductances. This means that the conductances of methanol has been subtracted.
[a]Molar ratio of DDQ:**1b** or **1c**.
[b]*C* (**1b** or **1c**) = 0.01 mol/L.
[c]Conductance of DDQ at 23 (50 °C) and 0.005 mol/L, 0.01 mol/L, and 0.02 mol/L was 11.18 (126.41), 23.81 (127.01), and 38.34 (131.41), respectively.

**Fig. 5.** The plot of conductances vs. DDQ–**1b** in different molar ratios at 23 and 50 °C.

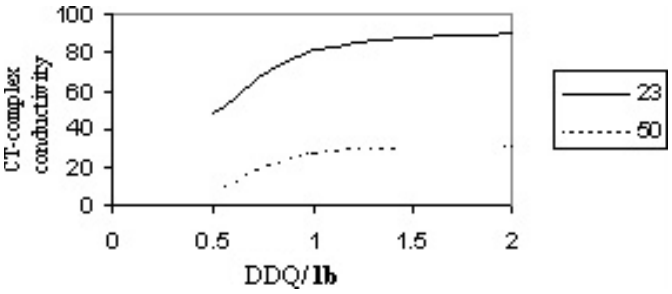
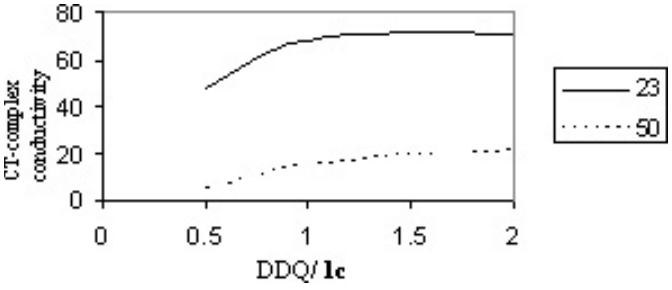



**Fig. 6.** The plot of conductances vs. DDQ–**1c** in different molar ratios at 23 and 50 °C.

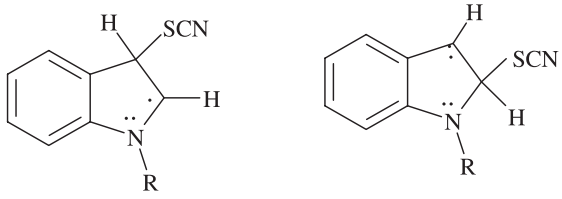



added DDQ (1.25 mmol). The reaction mixture was taken in pre-heated oil bath for the appropriate time according to Table 3. The progress of the reaction was monitored by TLC. The solvent was evaporated; the residue was diluted with water (10 mL) and extracted with chloroform (3 × 10 mL). The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure. The resulting crude product was purified by plate chromatography on silica gel (PLC; eluent: *n*-hexane–EtOAc, 9:1). Further recrystallization from petroleum ether – EtOAc gives the pure product (Table 3).

**3-Thiocyanatoindole (2a)**

Mp 105–106 °C (Lit. (11) 125–127 °C). IR ν: 3334 (NH), 2150 (SCN), 1435, 1410, 1232, 1095, 735 (N–H), 658 (C–S) cm$^{-1}$. $^1$H NMR ($CDCl_3$) δ: 7.29–7.42 (m, 4H, 4-, 5-, 6-, 7-H), 7.81 (d, 1H, *J* = 8.72 Hz, 2-H), 8.90 (brd s, 1H, NH). EI-MS *m/z* (%): 174 [M$^+$] (100), 148 [M$^+$ – CN] (63), 116 [M$^+$ – SCN] (28).

**Scheme 2.**




**2-Methyl-3-thiocyanatoindole (2b)**

Mp 99–101 °C (Lit. (11) 102–103 °C). IR ν: 3324 (NH), 2140 (SCN), 1582, 1540, 1455, 1408, 1228, 738 (N–H), 658 (C–S) cm$^{-1}$. $^1$H NMR ($CDCl_3$) δ: 2.58 (s, 3H, $CH_3$), 7.23–7.28 (m, 2H, 5-, 6-H), 7.34 (d, 1H, *J* = 7.63 Hz, 4-H), 7.69 (d, 1H, *J* = 7.52 Hz, 7-H), 8.41 (brd s, 1H, NH). EI-MS *m/z* (%): 188 [M$^+$] (100), 173 [M$^+$ – $CH_3$] (5), 161 [M$^+$ – HCN] (22), 146 [M$^+$ – HCN, – $CH_3$] (6), 117[M$^+$ – SCN, – $CH_3$] (15).

**1-Methyl-3-thiocyanatoindole (2c)**

Mp 83–84 °C. IR ν: 2145 (SCN), 1514, 1240, 748 (C–S), 661 cm$^{-1}$. $^1$H NMR ($CDCl_3$) δ: 3.82 (s, 3H, $CH_3$), 7.31–7.41 (m, 4H, 4-, 5-, 6-, 7-H), 7.81 (d, 1H, *J* = 7.56 Hz, 2-H). EI-MS *m/z* (%): 188 [M$^+$] (100), 173 [M$^+$ – $CH_3$] (37), 162 [M$^+$ – CN] (27), 146 [M$^+$ – HCN, – $CH_3$] (40), 130 [M$^+$ – SCN] (12).

**5-Bromo-3-thiocyanatoindole (2d)**

Mp 127–129 °C. IR ν: 3321 (NH), 2122 (SCN), 1452, 1408, 1106, 794 (N–H), 654 (C–S), 601 cm$^{-1}$. $^1$H NMR ($CDCl_3$) δ: 7.31 (d, 1H, *J* = 8.68 Hz, 7-H), 7.41 (dd, 1H, *J* = 8.65 Hz, *J* = 1.71 Hz, 6-H), 7.53 (d, 1H, *J* = 2.79 Hz, 4-H), 7.93 (s, 1H, 2-H), 8.72 (brd s, 1H, NH). EI-MS *m/z* (%): 253 [M$^+$] (27), 227 [M$^+$ – CN] (7), 173 [M$^+$ – Br] (100), 146 [M$^+$ – HCN, – Br] (19), 114 [M$^+$ – HSCN, – Br] (8).

**3-Thiocyanatocarbazole (2e)**

Mp 80–81 °C (Lit. (6) 76.5–78 °C). IR ν: 3295 (NH), 2155 (SCN), 2925, 1721, 1620, 1472, 1208, 1121, 1062, 734 (N–H), 702 (C–S) cm$^{-1}$. $^1$H NMR ($CDCl_3$) δ: 7.41–7.47 (m, 4H, 6-,7-,8-, 9-H), 7.53 (d, 1H, *J* = 8.55 Hz, 2-H), 7.59 (d, 1H, *J* = 3.1 Hz, 5-H), 7.68 (dd, 1H, *J* = 8.53 and 1.86 Hz, 2-H), 8.31 (brd S, 1H, NH). EI-MS *m/z* (%): 224 [M$^+$] (2), 191 [M$^+$ – SH] (4), 165 [M$^+$ – SCN, – H] (100).

**2-Thiocyanatopyrole (2fa)**

Liquid (Lit. (4) liquid). IR (film) ν: 3395 (NH), 2902, 2126 (SCN), 1462, 1381, 1115, 735 (N–H), 662 (C–S) $cm^{-1}$. $^1H$ NMR ($CDCl_3$) δ: 6.29 (dd, 1H, *J* = 5.91 and 2.91 Hz, 4-H), 6.66 (s, 1H, 3-H), 6.99 (s, 1H, 5-H), 8.87 (brd s, 1H, NH). EI-MS *m/z* (%): 124 [$M^+$] (100), 98 [$M^+$ – CN] (10).

**2,5-Dithiocyanatopyrole (2fb)**

Mp 97–99 °C (Lit. (10) 99–102 °C). IR ν: 3392 (NH), 2906, 2122 (SCN), 1623, 1381, 1105, 792 (N–H), 683 (C–S) $cm^{-1}$. $^1H$ NMR ($CDCl_3$) δ: 6.71 (d, 2H, *J* = 1.18 Hz, 3-, 4-H), 9.38 (brd s, 1H, NH). EI-MS *m/z* (%): 181 [$M^+$] (92), 154 [$M^+$ – HCN] (77), 123 [$M^+$ – SCN] (99), 96 [$M^+$ – HCN, – SCN] (100), 64 [$M^+$ – HSCN, – SCN] (27).

**4-Thiocyanatoaniline (2g)**

Mp 51–52 °C (Lit. (10) 51–52 °C). IR ν: 3375 ($NH_2$), 2144 (SCN), 2902, 1595, 1382, 1095, 795 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) δ: 3.95 (brd s, 2H, $NH_2$), 6.68 (d, 2H, *J* = 8.59 Hz, 2-, 6-H), 7.37 (d, 2H, *J* = 8.56 Hz, 3-, 5-H). EI-MS *m/z* (%): 150 [$M^+$] (33), 134 [$M^+$ – $NH_2$] (4), 123 [$M^+$ – HCN] (14), 91[$M^+$ – HSCN] (53).

**4-Thiocyanato-*N*-methylaniline (2h)**

Liquid. IR (film) ν: 3385 (NH), 2908, 2142 (SCN), 1596, 1508, 1305, 1181, 814 (N–H), 745 (C–S) $cm^{-1}$. $^1H$ NMR ($CDCl_3$) δ: 2.84 (s, 3H, $CH_3$), 4.12 (brd s, 1H, NH), 6.58 (d, 2H, *J* = 8.67 Hz, 2-, 6-H), 7.38 (d, 2H,, *J* = 8.64 Hz, 3-, 5-H). EI-MS *m/z* (%): 164 [$M^+$] (100), 149 [$M^+$ – $CH_3$] (820), 138 [$M^+$ – CN] (69), 105 [($M^+$ – SCN, – H] (60), 90 [$M^+$ – SCN, – H, – $CH_3$] (21), 77 [$M^+$ – $CH_3$, – NH, – SCN] (38).

**4-Thiocyanato-*N*,*N*-dimethylaniline (2i)**

Mp 71–72 °C (Lit. (4) 72–74 °C). IR ν: 2130 (SCN), 1585, 1504, 1368, 1079, 803 (C–S) $cm^{-1}$. $^1H$ NMR ($CDCl_3$) δ: 3.00 (s, 6H, $2CH_3$), 6.68 (d, 2H, *J* = 8.97 Hz, 2-, 6-H), 7.43 (d, 2H, *J* = 8.99 Hz, 3-, 5-H). EI-MS *m/z* (%): 178 [$M^+$] (100), 163 [$M^+$ – $CH_3$] (15), 152 [$M^+$ – CN] (29), 134 [$M^+$ – $N(CH_3)_2$] (11), 108 [$M^+$ – CN, – $N(CH_3)_2$] (23).

**2-Choloro-4-thiocyanatoaniline (2j)**

Mp 60–61 °C. IR ν: 3457 ($NH_2$), 3385 ($NH_2$), 2142 (SCN), 1627, 1595, 1482, 1153, 809, 702 (N–H), 668 (C–S), 563 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) δ: 4.39(brd s, 2H, $NH_2$), 6.77 (d,1H, *J* = 8.47 Hz, 6-H), 7.28 (dd, 1H, *J* = 8.46 and 2.14 Hz, 5-H), 7.50 (d, 2H, *J* = 2.14 Hz, 3-H). EI-MS *m/z* (%): 184 [$M^+$] (98), 158 [$M^+$ – CN] (78), 149 [$M^+$ – Cl] (98), 133 [$M^+$ – Cl, – $NH_2$] (18), 125 [$M^+$ – HSCN] (20). $C_7H_5N_2ClS$ (184.58) calcd.: C 45.54, H 2.71, N 15.17; found: C 45.48, H 2.69, N 15.13.

**3-Methoxy-4-thiocyanatoaniline (2k)**

Mp 99–100 °C. IR ν: 3368 ($NH_2$), 3415 ($NH_2$), 2121 (S–CN), 1627, 1593, 1462, 1327, 1218, 1047, 821 (N–H), 796 (C–S). $^1H$ NMR ($CDCl_3$) δ: 3.88 (s, 3H, $CH_3$), 3.99 (s, 2H, $NH_2$), 6.25 (d, 1H, *J* = 2.12 Hz, 2-H), 6.29 (dd, 1H, *J* = 8.29 and 2.24 Hz, 6-H), 7.30 (d, 1H, *J* = 8.30 Hz, 5-H). EI-MS *m/z* (%):180 [$M^+$] (100), 164 [$M^+$ – $NH_2$] (17), 149 [$M^+$ – $OCH_3$] (12), 110[$M^+$ – HCN, – $COCH_3$] (9), 91 [$M^+$ – SCN, – $OCH_3$] (13). $C_8H_8N_2OS$ (180.13) calcd.: C 53.34, H 4.44, N 15.54; found: C 53.40, H 4.41, N 15.49.

**4-Thiocyanatodiphenylamine (2la)**

Mp 62–64 °C. IR ν: 3332 (NH), 2132 (SCN), 1602, 1578, 1525, 1488, 1330, 820, 745 (N–H), 692 (C–S) $cm^{-1}$. $^1H$ NMR ($CDCl_3$) δ: 5.93 (brd s, 1H, NH), 7.03 (d, 2H, *J* = 8.65 Hz, 2-,6-H), 7.07 (t, 1H, *J* = 7.38 Hz, 4′-H), 7.14 (d, 2H, *J* = 7.82 Hz, 2′-, 6′-H), 7.34 (t, 2H, *J* = 7.84 Hz, 3′-, 5′-H), 7.43 (d, 2H, *J* = 8.67 Hz, 3-,5-H). EI-MS *m/z* (%): 226 [$M^+$] (100), 200[$M^+$ – CN] (30), 167 [$M^+$ – H, – SCN] (66), 77 [$Ph^+$] (36).

**4,4′-Dithiocyanatodiphenylamine (2lb)**

Mp 110–111 °C. IR ν: 3342 (NH), 2125 (SCN), 1582, 1516, 1482, 1335, 803 (N–H) $cm^{-1}$. $^1H$ NMR ($CDCl_3$) δ: 6.09 (brd s, 1H, NH), 7.12 (d, 4H, *J* = 8.68 Hz, 3-, 5-, 3′-, 5′-H), 7.49 (d, 4H, *J* = 8.68 Hz, 2-, 6-, 2′-, 6′-H). EI-MS *m/z* (%): 283 [$M^+$] (19), 257 [$M^+$ – CN] (4), 225 [$M^+$ – SCN] (23), 149[$M^+$ – PhSCN] (11), 122 [$M^+$ – PhSCN, – HCN] (22), 90 [$M^+$ – PhSCN, – HSCN] (4).

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