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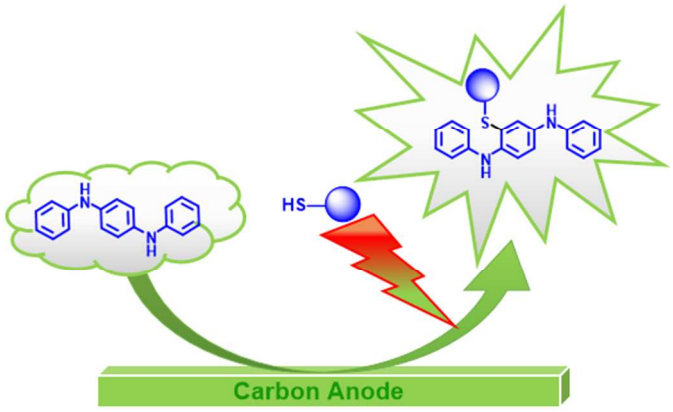
A green electrochemical method for the synthesis of new *N*,*N*'-diphenylbenzene-1,4-diamine derivatives

Davood Nematollahi,* Saeideh Mahdinia, Sajad Kaihani and Hamid Salehzadeh

Graphical Abstract

A green method for the synthesis of new organosulfur derivatives based on the Michael reaction of electrochemically generated *N*,*N*'-diphenyl-*p*-quinonediimine with some thiols is described.



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A green method for the synthesis of new organosulfur derivatives of *N,N'*-diphenylbenzene-1,4-diamine (**2a-2e**) based on the Michael reaction of electrochemically generated *N,N'*-diphenyl-*p*-quinonediimine with 2-mercaptopyridine, 1*H*-1,2,4-triazole-3-thiol, 1-phenyl-1*H*-tetrazole-5-thiol, 2-mercaptobenzoxazole and 2-mercaptobenzothiazole as nucleophiles in a water/ethanol (25/75, v/v) mixture is described. The thioethers (**2a-2e**) were synthesized in high yields, without toxic reagents and solvents at a carbon electrode using an environmentally friendly method with high atom economy.

Introduction

1,4-Phenylenediamines are important compounds in the manufacture of dyes, pharmaceuticals, polymers, and other industrial products.[1] They are also very susceptible to oxidative polymerization via oxidation of amino groups (one or two) to give linear azopolymers, ladder polyphenazines, poly aminoanilines, and phenazine/iminoquinonoid-unit containing polymers.[2] In addition, they are extensively used in the manufactory of azo dyes.[3] Furthermore, they are used as antioxidant agent in various vulcanized rubber and they provide a preferable protection.[4] Among these, *N,N'*-substituted *p*-phenylenediamines, represent the most important group of antioxidants[5] used in rubber industry[6] and reducing NO_x emissions in the diesel engines.[7] It is well known that antioxidants (e.g. *N,N'*-substituted *p*-phenylenediamines) interact with free radicals in various ways, including hydrogen abstraction, addition of a radical species to the antioxidant and simple electron transfer reactions.[5]

It should be noted that, in pathways 1-3, the products are less reactive than the initial radical species. The last pathway includes electron transfer between oxidizing radical species and reducing substrate. In this context, the antioxidant activity of six *N,N'*-substituted *p*-phenylenediamines in polyisoprene rubber matrix was studied by differential scanning calorimetry and shown that

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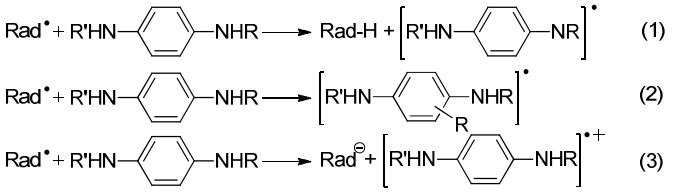


antioxidant activity of these compounds is dependent on their structure.[8] In addition, some other studies indicate that in the mechanism of antioxidant action of *N,N'*-substituted *p*-phenylenediamines instead of the classical reaction pathway leading to the *N,N'*-substituted *p*-quinonediimines.[9] Their studies indicated that the structure of the individual *N,N'*-substituted *p*-phenylenediamines, is a major determinant in predicting antioxidant activities of these compounds.

Despite of numerous studies concerning the oxidation of *N,N'*-substituted *p*-quinonediimines, particularly *N,N'*-diphenylbenzene-1,4-diamine (**DPD**) as a model compound in the field of antioxidant activities,[4-9] synthesis of organic compounds[10] and synthesis of conducting polymers,[11] there is no report on the electrochemical functionalization of **DPD**. Following our strategy for synthesis of organic compounds under green conditions,[12] we wish to study the functionalization

of **DPD** and to describe a one-pot and straightforward protocol for the synthesis of some new organosulfur derivatives of *N*,*N'*-diphenylbenzene-1,4-diamine (**2a-2e**). This idea prompted us to investigate the electrochemical oxidation of **DPD** in the presence of 2-mercaptopyridine (pyridine-2-thiol) (**1a**), 1*H*-1,2,4-triazole-3-thiol (**1b**), 1-phenyl-1*H*-tetrazole-5-thiol (**1c**), 2-mercaptobenzoxazole (**1d**) and 2-mercaptobenzothiazole (**1e**) (Fig. 1). This method represents a facile electrochemical process for the synthesis of some thioethers (**2a-2e**) in high yields and purities under green conditions, without toxic reagents and solvents in a divided cell using an environmentally friendly method at a carbon electrode.

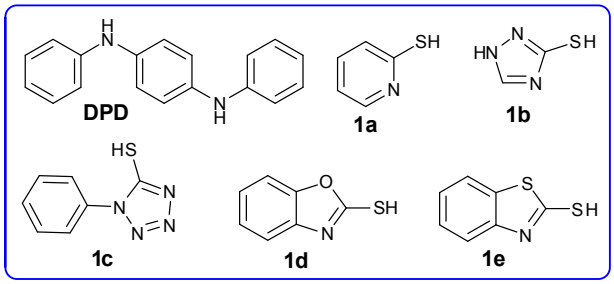


Fig. 1 Structure of **DPPD** and other organosulfur compounds (**1a**-**1e**).

Results and discussion

Cyclic voltammograms of a solution of *N*,*N*'-diphenyl-*p*-phenylenediamine (**DPD**) in water (phosphate buffer, pH = 2.0, *c* = 0.2 M)/ethanol (25/75, v/v) mixture, in the absence and the presence of 2-mercaptopyridine (**1a**) are shown in Figure 2. Curve a which is attributed to the electrochemical oxidation of **DPD** shows an anodic peak (A_1) at 0.24 V corresponding cathodic peak (C_1) at 0.15 V, which corresponds to the transformation of **DPD** to *N*,*N*'-diphenyl-*p*- quinonediimine (**DQD**) and vice versa within a quasi-reversible two-electron process.[13] A measure of reversibility is provided by the ratio of the cathodic to anodic peak current (I_{pC1}/I_{pA1}), which is closer to 1. This confirms the stability of the electrogenerated **DQD** under the experimental conditions. In other words, the side reactions, such as hydroxylation,[14] dimerization[15] or oxidative ring cleavage[16] that involve quinones, quinoneimines or quinonedidiimines, are too slow to be observed at the time scale of cyclic voltammetry.[14-16] The oxidation of **DPD** in the presence of **1a** as a nucleophile was studied in some detail (Fig. 2, curve b). As can be seen from this figure, the cathodic peak (C_1) decreases and a new anodic peak (A_2) appeared in more positive potentials. Under these conditions, the ratio of the cathodic to anodic peak current (I_{pC1}/I_{pA1}), is less than 1. It decreases with decreasing scan rate and increasing **1a** concentration (Fig. 2, inset), indicating that the product of the electron transfer (**DQD**) is undergoing a following chemical reaction.[17] In Fig. 2, curve c is related to 2-mercaptopyridine (**1a**) itself. The comparison of cyclic voltammogram of **1a** with curve b shows that anodic peak A_2 is due to the oxidation of **1a**.

These studies were followed by controlled potential coulometry (cpc) of **DPD** (0.25 mmol) in the presence of **1a** (0.25 mmol) in water (phosphate buffer, pH = 2.0, *c* = 0.2 M)/ethanol (25/75, v/v) mixture at the potential of peak A_1. The number of transferred electrons was calculated from the charge that had accumulated when the current fell below 5% of its initial value. The calculated number of transferred electrons per molecule of **DPD** was 2.

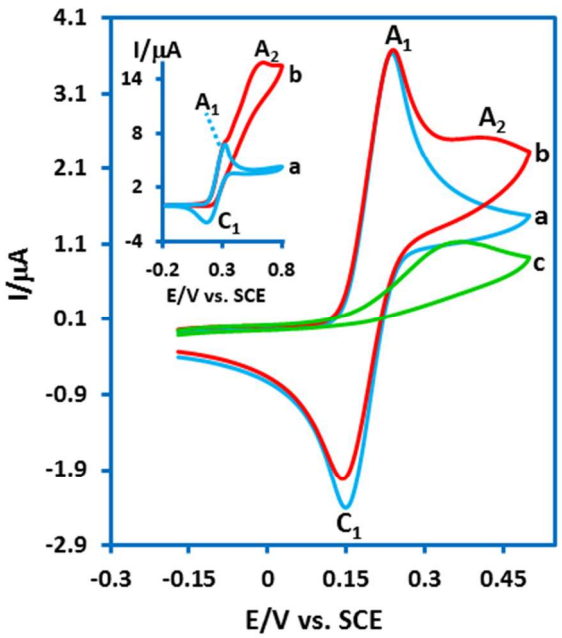


Fig. 2 Cyclic voltammograms of: (a) **DPD** (1.0 mM), (b) **DPD** (1.0 mM) in the presence of 2-mercaptopyridine (**1a**) (1.0 mM) and (c) 2-mercaptopyridine (**1a**) (1 mM), at a glassy carbon electrode in water(phosphate buffer, pH = 2.0, *c* = 0.2 M)/ethanol (25/75, v/v) mixture. Inset: (a) **DPD** (1.0 mM), (b) **DPD** (1.0 mM) in the presence of 2-mercaptopyridine (**1a**) (5.0 mM).Scan rate: 10 mV s^{-1}. T = 25 ± 1 °C.

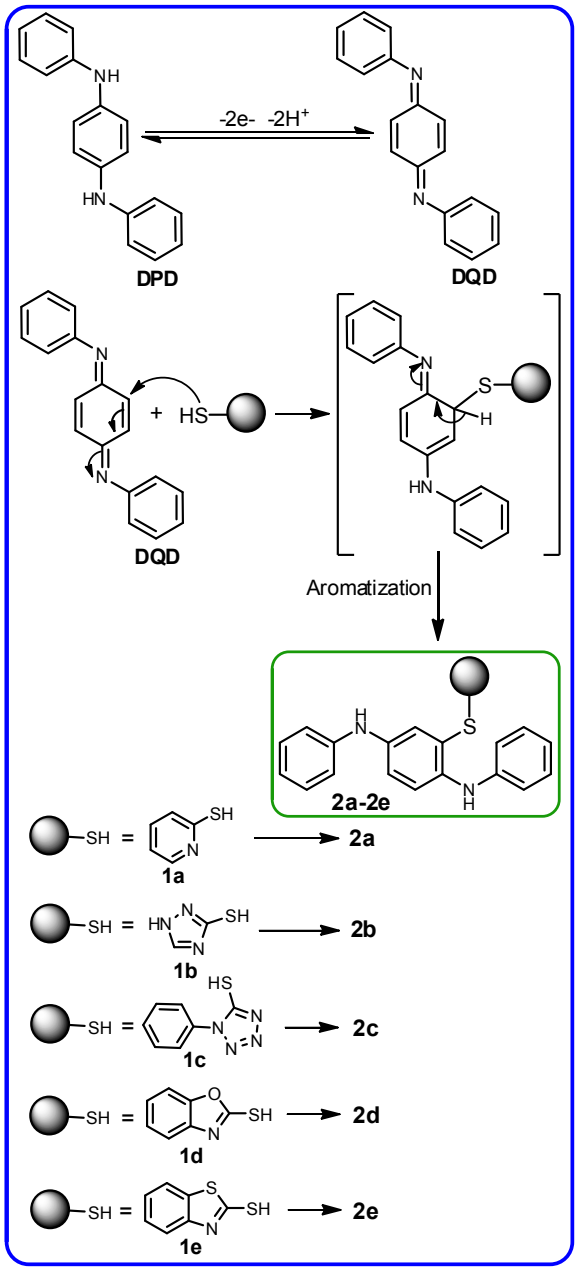
Diagnostic criteria of cyclic voltammetry and controlled potential coulometry accompanied by ^{1}H NMR, ^{13}C NMR and MS spectra of final product allow us to propose the following mechanism for the electrochemical oxidation of **DPD** in the presence of **1a** (Scheme 1). According to our results, the Michael addition reaction of **1a** with electrogenerated **DQD** followed by the aromatization of the resulting intermediate to give **2a** as the final product. The same results were obtained for the other sulfur compounds given in Fig. 2 (data not shown).

The preparative synthesis of **2a-2e** was performed in potentiostatic condition by oxidation of **DPD** in the presence of thioles **1a-1e**, at 0.25 V versus SCE potential on a graphite anode in a divided cell. More detail is described in the Experimental Section.

In order to the investigation of the electrochemical properties of the isolated products, the cyclic voltammetric behaviour of **2b** was examined (Fig. 3, curve b). As can be seen, voltammogram exhibits a quasi-reversible system with $E_{1/2}$= 0.21 V vs. SCE. Comparing the half wave potential of cyclic voltammogram of **2b** with that of **DPD** ($E_{1/2}$= 0.24 V vs. SCE), shows that half wave potential of product (**2b**) is less

than **DPD**. This may increase the antioxidant activity of **2b** in comparison with **DPD.**

It should be noted that, different to cyclic voltammograms of **DPD** in pHs ≥ 2 (Fig. 1, curve a), at pH values ≤ 1, cyclic voltammogram of **DPD** shows more complex behavior. In this condition the cyclic voltammograms of **DPD** exhibits two anodic peaks A_I and A_{II} in the positive-going scan and two corresponding cathodic peaks C_I and C_{II} in the negative-going scan (Fig. 4). The anodic peaks A_1 and A_2 correspond to two successive oxidations, the first one of **DPD** to radical cation **DPD**$^{\cdot+}$ (or **DPD**$^{\cdot}$) and the second one of **DPD**$^{\cdot+}$ (or **DPD**$^{\cdot}$) to *N*,*N*'-diphenyl-*p*- quinonediimine (**DQD**). The cathodic peaks C_2 and C_1 correspond respectively to the one-electron reduction of **DQD** to **DPD**$^{\cdot+}$ (or **DPD**$^{\cdot}$) and to the one-electron reduction of **DPD**$^{\cdot+}$ (or **DPD**$^{\cdot}$) to **DPD**.



Scheme 1. Proposed mechanism for the electrochemical oxidation of **DPD** in in the presence of thioles **1a-1e.**

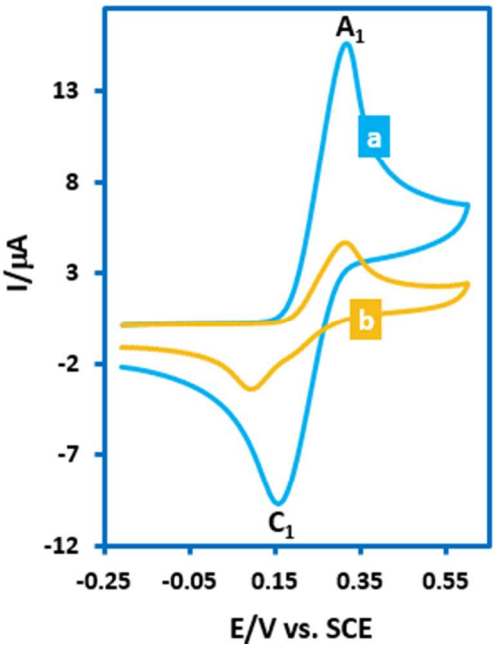


Fig. 3. (a) Cyclic voltammogram of **DPD** (1.0 mM), (b) Cyclic voltammogram of saturated solution of product **2b** at a glassy carbon electrode in water (phosphate buffer, pH = 2.0, *c* = 0.2 M)/ethanol (25/75, v/v) mixture. Scan rate: 100 mV s^{-1}. T = 25 ± 1 °C.

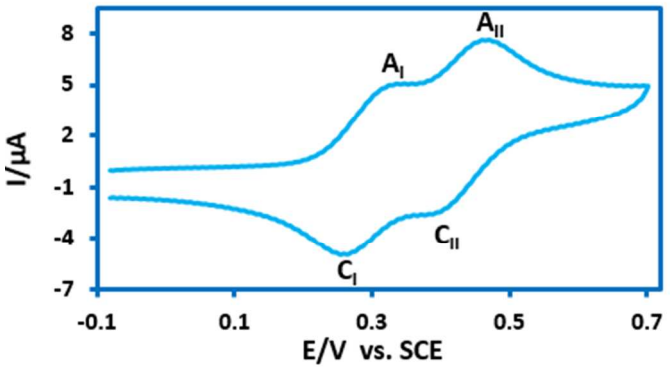


Fig. 4 Cyclic voltammogram of **DPD** (1.0 mM), at a glassy carbon electrode in water (HCl 0.1M)/ethanol (25/75, v/v) mixture. Scan rate: 10 mV s^{-1}. T = 25 ± 1 °C.

From the point of view of green chemistry, the presented method has some important advantages. High atom economy (>99%), use of electricity as energy instead of oxidative reagents, clean synthesis, use of aqueous media (75% water) instead of organic solvents, work in room temperature, one-step reaction, and pressure and technical feasibility are of preeminent green advantages.

Conclusion

To the best of our knowledge, only a few reports have appeared on the functionalization of **DPD**.[18] On the other hand, this is the

first report of synthesis **DPD** derivatives by electrochemical method. The results of this work show that **DPD** is oxidized to *N,N'*-diphenyl-*p*-quinonediimine (**DQD**) within a quasi-reversible two-electron process.[13]. The formed **DQD** is attacked by thioles **1a-1e** to form thioethers **2a-2e** in high yields and purities. The reaction mechanism for anodic oxidation of **DPD** in the presence of **1a-1e** is presented in Scheme 1. The present method for the synthesis of thioethers **2a-2e** has several advantages. (a) This process is practically convenient to carry out and can be performed in aqueous solution/ethanol mixture, at room temperature and atmospheric pressure. (b) Neither catalyst nor organic/inorganic oxidizing agents are necessary and the reaction can be performed in one-pot, under green and mild conditions. (c) The synthesized compounds (**2a-2e**), may show efficient antioxidant activity. To conclude, while the reactions are performed on a mmol scale, there is little difficulty in producing larger quantities by using larger cells.

Experimental

Cyclic voltammetry, controlled-potential coulometry and preparative electrolysis were performed using an Autolab model PGSTAT 20 potentiostat/galvanostat. The working electrode used in the voltammetry experiments was a glassy carbon disc (1.8 mm^2 area) and platinum wire was used as counter electrode. The working electrode used in controlled-potential coulometry and synthesis was an assembly of four carbon rods (31 cm^2) and large platinum gauze constitute the counter electrode. The working electrode potentials were measured versus SCE (all electrodes from AZAR electrode). *N,N'*-Diphenylbenzene-1,4-diamine, 2-mercaptopyridine, 1*H*-1,2,4-triazole-3-thiol, 1-phenyl-1*H*-tetrazole-5-thiol, 2-mercaptobenzoxazole and 2-mercaptobenzothiazole and other solvents and reagents were reagent-grade materials from Aldrich. The glassy carbon electrode was polished using alumina slurry (from Iran Alumina Co.)

General procedure for synthesis of 2a-2e

In a typical procedure, a solution (80 mL) of water (phosphate buffer, pH = 2.0, *c* = 0.2 M)/ethanol (25/75, v/v) containing **DPD** (0.25 mmol, 0.0664 g) and 0.25 mmol of thiols (**1a**: 0.0281 g, **1b**: 0.0261 g, **1c**: 0.0455 g, **1d**: 0.0398 g, **1e**: 0.0431) was electrolyzed in a divided cell at 0.20 V vs. SCE. The electrolysis was terminated when the decay of the current became more than 95%. The solid precipitated was collected by filtration and was washed several times with water. After drying, the residual solid dissolved in acetone and filtered. Acetone was removed under vacuum and the residual washed with diethylether and dried. The products were characterized by IR, ^{1}H NMR, ^{13}C NMR and MS.

***N,N'*-Diphenyl-2-(pyridin-2-ylthio)benzene-1,4-diamine (2a) $C_{23}H_{19}N_3S$.** Isolated yield: 77% (0.0711 g), mp 174-175 ^{o}C; ^{1}H NMR (250 MHz, DMSO-d_6) δ: 5.32 (b, 1H), 6.53 (d, *J* = 8.4 Hz, 1H), 6.83 (t, 1H), 6.93-7.13 (m, 6H), 7.17-7.34 (m, 7H), 7.61 (t, 1H), 8.00 (d, *J* = 4.7 Hz, 1H), 8.65 (b, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 111.8, 115.7, 116.8, 118.0, 121.1, 125.5, 126.4, 129.2, 129.9, 130.2, 131.3, 134.9, 141.7, 142.2, 144.9, 154.4; IR (KBr) ν: 3439, 3300, 3059, 1632, 1604, 1588, 1525, 1485, 1384, 1324, 1244, 1166, 1122, 1033, 761, 695 cm^{-1}; MS (*m/z*) (relative intensity): 369 [$M^{+\cdot}$] (29), 336 (42), 313 (23), 285 (15), 260 (18), 236 (27), 211 (14), 169 (57), 139 (31), 111 (45), 83 (63), 57 (100).

2-((1*H*-1,2,4-triazol-3-yl)thio)-*N,N'*-diphenylbenzene-1,4-diamine (2b), $C_{20}H_{17}N_5S$. Isolated yield: 72% (0.0647 g), mp 248-250 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 6.73-6.84 (m, 7H), 7.05 (s, 2H), 7.15 (t, 5H), 7.67 (s, 1H), 8.60 (b, ~ 1H); ^{13}C NMR (150 MHz, DMSO-d_6) δ: 114.8, 116.2, 116.7, 124.2, 129.4, 137.0, 144.9, 146.1, 156.4; IR (KBr) ν: 3282, 3119, 3067, 1598, 1532, 1496, 1467, 1380, 1312, 1282, 1237, 1175, 999, 970, 866, 740, 690; cm^{-1}; MS (*m/z*) (relative intensity): 359 [$M^{+\cdot}$] (66), 289 (13), 260 (100), 183 (75), 167 (65), 154 (21), 139 (15), 128 (24), 77 (58), 55 (43).

***N*^{1},*N*^{4}-Diphenyl-2-((1-phenyl-1H-tetrazol-5-yl)thio)benzene-1,4-diamine (2c), $C_{26}H_{20}N_6S$.** Isolated yield: 64% (0.0698 g), mp 133-134 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 6.68 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 7.2 Hz, 1H), 6.83 (t, 1H), 7.01 (m, 3H), 7.08-7.16 (m, 4H), 7.23 (t, 2H), 7.50 (s, 1H), 7.61 (m, 5H), 8.20 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 115.1, 116.5, 116.6, 118.6, 119.1, 119.8, 120.8, 123.8, 124.9, 125.2, 128.9, 129.2, 129.7, 130.6, 133.1, 134.9, 140.1, 143.2, 145.7, 152.6; IR (KBr) ν: 3375, 3051, 2924, 2853, 1599, 1498, 1384, 1312, 1262, 1177, 1111, 1082, 1016, 868, 748, 693, 497 cm^{-1}; MS (*m/z*) (relative intensity): 436 [M +H] (12), 394 (27), 290 (96), 250 (15), 199 (41), 118 (100), 91 (49), 51 (28).

2-(Benzo[d]oxazol-2-ylthio)-*N,N'*-diphenylbenzene-1,4-diamine (2d), $C_{25}H_{19}N_3OS$. Yield, 52% (0.0532 g), mp 104-106 ^{o}C; ^{1}H NMR (500 MHz, DMSO-d_6) δ: 6.96 (d, 2H), 7.03 (s, 2H), 7.17 (t, 2H), 7.24-7.32 (m, 10H), 7.50 (d, *J* = 7.7 Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ: 112.5 116.2, 116.7, 118.2, 119.7, 120.7, 121.8, 122.2, 123.2, 124.2, 129.1, 129.2, 131.6, 141.3, 141.8, 152.3, 153.9; IR (KBr) ν: 3388, 3032, 2922, 1599, 1512, 1494, 1449, 1310, 1226, 1177, 1131, 1094, 929, 874, 820, 743, 693; cm^{-1}; MS (*m/z*) (relative intensity): 409 [$M^{+\cdot}$] (100), 392 (5), 376 (4), 317 (3), 289 (35), 256 (6), 186 (5), 167 (6), 154 (8), 91 (5), 77 (13).

2-(Benzo[*d*]thiazol-2-ylthio)-*N,N'*-diphenylbenzene-1,4-diamine (2e) $C_{25}H_{19}N_3S_2$. Yield, 65% (0.0692 g), mp 76-77 ^{o}C; ^{1}H NMR (400 MHz, acetone-d_6) δ: 6.88 (m, 3H), 7.08-7.12 (m, 8H), 7.17-7.28 (m, 4H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 5.2 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ: 110.7, 111.0, 112.5, 117.7, 117.9, 118.5, 119.6, 120.9, 121.0, 124.6, 125.9, 129.4, 129.9, 130.0, 131.0, 137.9, 149.5; IR (KBr) ν: 3388, 3037, 1597, 1512, 1496, 1456, 1426, 1312, 1243, 1077, 1034, 1013, 828, 751, 693, 669, 604 cm^{-1}; MS (*m/z*) (relative intensity): 425 [$M^{+\cdot}$] (26), 393 (37), 350 (50), 333 (35), 260 (59), 198 (11), 184 (47), 167 (100), 154 (28), 128 (30), 109 (13), 91 (12), 77 (27).

Acknowledgements

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