Polyfunctional heteroaromatics: a route to dicyanomethylene thiazoles based on the reaction of \(\alpha\)-thiocyanatoketones with malononitrile

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Abstract
Reactions of \(\alpha\)-S-cyanothioketones 6a-c with malononitrile were observed to form 2-(thiazol-2(3H)-ylidene)malononitrile derivatives 7a-c. The thiazole products readily react with aromatic diazonium salts to yield 2-(5-phenylazo-3H-thiazol-2-ylidene)-malononitrile derivatives 8a-c. The malononitrile derivative 8c undergoes a condensation with DMF/DMA to yield thiazolo[5,4-c]pyridazine 12. Reactions of 7a-c with hydrazine hydrate lead to the generation of diaminopyrazoles 9a-c, which react with enaminone 13 to yield the corresponding thiazolylpyrazolo[1,5-a]pyrimidines 14. In addition, reaction of the malononitrile derivative 8a with benzenediazonium chloride readily affords the coupling product 10.

Keywords: \(\alpha\)-Thiocyanatoketones, malononitrile, thiazoles, thiazolo[5,4-c]pyridazine, diaminopyrazoles, thiazolylpyrazolo[1,5-a]pyrimidines

Introduction

The considerable biological activity observed for pyridazines and condensed pyridazines has stimulated considerable recent interest in the synthesis of these heterocyclic compounds.\textsuperscript{1-4} Recent developments in this area have been reviewed by one of us.\textsuperscript{5} The results of earlier efforts have shown that condensation reactions of \(N\)-aryl-\(\alpha\)-hydrazonoketones 1 with active methylene nitriles can be employed to prepare \(N\)-arylsubstituted-pyridazinones and pyridazine-6-imines.\textsuperscript{6-8} It is assumed that the pathway for this process involves initial condensation of the \(\alpha\)-hydrazonoketones with the active methylene substances to yield conjugated hydrazone-esters 2 that readily cyclize to produce 3. In contrast, Abdelrazek and Fadda reported that the \(S\)-cyanothio unsaturated bis-nitrile 4 undergoes coupling with aromatic diazonium salts to yield the diazo compounds 5, which are reported to be stable substances (Scheme 1).\textsuperscript{9} We have already noted
that this observation should be reevaluated since, if correct, it would represent the only reported example of an acyclic diazo compound of this type.\textsuperscript{5}

\[
\begin{align*}
\text{Scheme 1}

\text{Herein, we describe the results of an investigation of this process and, which has led to a reassignment of the structure of 5 to that of the thiazolidine derivatives 7a-c. The recognition of the revised structures led to further work that culminated in the synthesis of a variety of novel condensed thiazolylpyrazolo[1,5-\textit{a}]pyrimidines that are structurally related to zaleplone.}\textsuperscript{10}

\end{align*}
\]
Initially, we explored the report by Abdelrazek et al.\textsuperscript{9} which suggested that the \( S \)-cyanothio unsaturated bis-nitrile \( 4 \) is obtained via condensation reaction of \( \alpha \)-thiocyanatoketones \( 6a \) with malononitrile in presence of piperidine. Indeed, we observed that this reaction affords a product with the same molecular formula of \( 5 \), reported by the authors.\textsuperscript{9} However, careful analysis of spectroscopic data indicated that the product of this process has the thiazolidine structure \( 7a \). For example, the \(^1\text{H} \) and \(^{13}\text{C} \) NMR spectra of the product contain no resonances that correspond to protons linked to \( sp^3 \) hybridized carbons or \( sp^3 \) carbons. The obtained data matched to those expected for the thiazolidine structure \( 7a \). In addition, we observed that reactions of the \( \alpha \)-\( S \)-cyanothioketones \( 6b,c \) with malononitrile afforded dicyanomethylene thiazolidines, whose spectroscopic properties matched those of \( 7b,c \) (cf. Scheme 2).

\[
\begin{align*}
\text{PhN} & \equiv \text{NCl}^- \\
& \text{reflux 20 h} \\
& \text{EtOH} \\
\text{NH}_2\text{NH}_2 \\
& \text{EtOH} \\
\text{reflux 20 h} \\
R &= \text{Ph} \\
\text{NH}_2\text{NH}_2 \\
& \text{EtOH} \\
\text{reflux 20 h} \\
R &= \text{Ph} \\
\text{PhN} & \equiv \text{NCl}^- \\
\end{align*}
\]

\( 7a-c \)

\[
\begin{align*}
\text{NH}_2\text{NH}_2 \\
& \text{EtOH} \\
\text{reflux 20 h} \\
\text{R} &= \text{Ph} \\
\text{PhN} & \equiv \text{NCl}^- \\
\end{align*}
\]

\( 8a-c \)

\[
\begin{align*}
\text{NH}_2\text{NH}_2 \\
& \text{EtOH} \\
\text{reflux 20 h} \\
\text{R} &= \text{Ph} \\
\text{PhN} & \equiv \text{NCl}^- \\
\end{align*}
\]

\( 9a-c \)

\[
\begin{align*}
\text{NH}_2\text{NH}_2 \\
& \text{EtOH} \\
\text{reflux 20 h} \\
\text{R} &= \text{Ph} \\
\text{PhN} & \equiv \text{NCl}^- \\
\end{align*}
\]

\( 10 \)

\[
\begin{align*}
\text{PhN} & \equiv \text{NCl}^- \\
\text{reflux 20 h} \\
\text{EtOH} \\
\text{NH}_2\text{NH}_2 \\
& \text{EtOH} \\
\text{reflux 20 h} \\
\text{R} &= \text{Ph} \\
\text{PhN} & \equiv \text{NCl}^- \\
\end{align*}
\]

\( 7a-c \)

\[
\begin{align*}
\text{NH}_2\text{NH}_2 \\
& \text{EtOH} \\
\text{reflux 20 h} \\
\text{R} &= \text{Ph} \\
\text{PhN} & \equiv \text{NCl}^- \\
\end{align*}
\]

\( 8a-c \)

In further exploratory studies, we observed that \( 7a-c \) react with benzenediazonium chloride to generate the diazo compounds \( 8a-c \) and that \( 8a \) can be transformed to the diaminopyrazoles \( 10 \) by reaction with hydrazine hydrate. The pyrazolo-thiazolidines, related to \( 10 \), were also produced by direct reactions of \( 7a-c \) with hydrazine hydrate and subsequent coupling of the diaminopyrazolyl thiazole products \( 9a-c \) with benzenediazonium chloride (cf. Scheme 3).

\[
\begin{align*}
\text{DMFDMA} \\
& \text{reflux 14 hr} \\
R &= \text{CH}_3 \\
\text{reflux 14 hr} \\
\end{align*}
\]

\( 8c \)

\[
\begin{align*}
\text{Me}_2\text{N} \\
\text{PhN} & \equiv \text{NCl}^- \\
\text{reflux 14 hr} \\
\text{reflux 14 hr} \\
\text{PhN} & \equiv \text{NCl}^- \\
\end{align*}
\]

\( 11 \)

\[
\begin{align*}
\text{PhN} & \equiv \text{NCl}^- \\
\text{reflux 14 hr} \\
\text{reflux 14 hr} \\
\text{PhN} & \equiv \text{NCl}^- \\
\end{align*}
\]

\( 12 \)

\[
\begin{align*}
\text{Me}_2\text{N} \\
\text{PhN} & \equiv \text{NCl}^- \\
\text{reflux 14 hr} \\
\text{reflux 14 hr} \\
\text{PhN} & \equiv \text{NCl}^- \\
\end{align*}
\]

\( 11 \)

\[
\begin{align*}
\text{PhN} & \equiv \text{NCl}^- \\
\text{reflux 14 hr} \\
\text{reflux 14 hr} \\
\text{PhN} & \equiv \text{NCl}^- \\
\end{align*}
\]

\( 12 \)
In addition, we found that reaction of 8c with DMF/DMA at reflux for 14 h afforded the thiazolo[5,4-c]pyridazine 12 in 80% yield. This process is assumed to follow a route in which 8c was initially converted to the enamine derivative 11 that then underwent sequential electrocyclization and dimethylamine elimination to form 12 (cf. Scheme 4).

Scheme 5

Figure 1. Plot of the x-ray crystallographic data of pyrazolo[1,5-a]pyrimidine 14.
Furthermore, diaminopyrazolylthiazoles 9c participate in an efficient condensation reaction with enaminone 13 to yield thiazolylpyrazolo[1,5-a]pyrimidines 14. X-ray crystallographic analysis of this product showed unambiguously that it has the structure 14 (Figure 1) rather than that of the regioisomer 15 (Scheme 5). It is important to note that 14 exists in a planar conformation, which suggests that the amino group is hydrogen bonded to thiazole ring nitrogen.

Conclusions

In conclusion, the results of this effort have led to the revised assignment of the thiazolidine structures for 7a-c and a demonstration that these substances serve as versatile precursors to uniquely substituted pyrazolo[1,5-a]pyrimidines and thiazolylpyrazolo[1,5-a]pyrimidines.

Experimental Section

General. Melting points are reported uncorrected and were determined with a Sanyo (Gallaenkamp) instrument. Infrared spectra were recorded using KBr pellets and a Perkin-Elmer 2000 FT–IR instrument. 1H and 13C NMR spectra were determined by using a Bruker DPX instrument at 400 MHz for 1H NMR and 100 MHz for 13C NMR and either CDCl3 or DMSO-d6 solutions with TMS as internal standards. Chemical shifts are reported in δ (ppm). Mass spectra were measured using VG Autospec Q MS 30 and MS 9 (AEI) spectrometer, with the EI (70 EV) mode. Elemental analyses were carried out by using a LEOCHNS-932 Elemental Analyzer.

General procedure for the syntheses 7a-c
Solutions of malononitrile (0.66 g, 0.01 mol) and α-thiocyanatoketones 5a-c (0.01 mol) in ethanol (15 mL) containing piperidine (5 drops) were stirred at reflux for 3-4 h (completion assessed by TLC, 1:1 ethyl acetate-petroleum ether). The solid products, produced by pouring the reaction mixtures into ice-water and subsequent separation by filtration, were crystallized from EtOH (green crystals).

2-(4-Phenylthiazol-2(3H)-ylidene)malononitrile (7a). Yield 93 %; mp 275-76 ºC; Anal. calcd. for C12H7N3S (225.27): C, 63.98; H, 3.13; N, 18.65; S, 14.23. Found: C, 63.94; H, 3.31; N, 18.45; S, 13.92; IR (KBr): v max = 3147 (NH), 2210 (CN), 2175 (CN); 1H-NMR (DMSO): δ, ppm = 7.33 (s, 1H, CH), 7.45-7.49 (m, 3H, Ar-H), 7.71-7.72 (m, 2H, Ar-H), 13.23 (br, 1H, NH, D2O exchangeable); 13C-NMR (DMSO): δ, ppm = 172.27, 143.70, 130.01, 129.12(2C), 128.92, 127.51 (2C), 127.64 117.75, 105.93 (2CN). MS: m/z (%) 225 (M+, 100), 180 (20), 134 (45), 108 (10), 102 (15), 89 (15), 77 (10).

2-(4-(4-Chlorophenyl)thiazol-2(3H)-ylidene)malononitrile (7b). Yield 95 %; mp 270-72 ºC; Anal. calcd. for C12H6ClN3S (259.7): C, 55.50; H, 2.33; N, 16.18; S, 14.34. Found: C, 55.32; H, 2.15; N; 15.95; S, 14.52; IR (KBr): v max = 3155 (NH), 2219 (CN), 2185 (CN); 1H-NMR
(DMSO): $\delta$, ppm = 7.38 (s, 1H, CH), 7.53-7.55 (d, 2H, Ar-H), 7.75-7.77 (d, 2H, Ar-H), 13.01 (br, 1H, NH, D$_2$O exchangeable); $^{13}$C-NMR (DMSO): $\delta$, ppm = 171.70, 142.49, 133.98, 128.71 (2C), 128.62 (2C), 127.82, 117.43, 115.75, 106.10 (2CN). MS: $m/z$ (%) 261 (M$^{+2}$, 40), 260 (M$^{+}$, 30), 259 (M$^{+}$, 100), 224 (10), 168 (30), 159 (10), 133 (15), 89 (15), 75 (5).

2-(4-methylthiazol-2(3H)-ylidene)malononitrile (7c). Yield 85 %; mp 290-91 ºC; Anal. calcd. for C$_7$H$_5$N$_3$S (163.2): C, 51.52; H, 3.09; N, 25.75; S, 19.64. Found: C, 51.26; H, 3.12; N; 25.54; S, 19.27; IR (KBr): $\nu_{max}$ = 3160 (NH), 2179 (2CN); $^{1}$H-NMR (DMSO): $\delta$, ppm = 2.17 (s, 3H, CH$_3$), 6.71 (s, 1H, CH), 13.1 (br, 1H, NH, D$_2$O exchangeable); $^{13}$C-NMR (DMSO): $\delta$, ppm = 170.10, 142.54, 105.93 (2CN), 87.68, 16.54. MS: $m/z$ (%) 163 (M$^{+}$, 100), 136 (20), 118 (30), 98 (10), 71 (50).

**General procedure for syntheses of 8a-c**

A cold solution of benzenediazonium chloride (0.01 mol) was prepared by adding a solution of sodium nitrite (0.7 g in 10 mL H$_2$O) to a cold solution of aniline hydrochloride (0.93 g, 0.01 mol of aniline in 5 mL concentrated HCl) with stirring at room temperature. The resulting solution was then added to cold solutions of 7a-c (0.01 mol) in ethanol (50 mL) containing sodium acetate (2 g). The reaction mixtures was stirred for 1 h and then filtered. The solid products were crystallized from EtOH to give the products as red crystals.

2-(4-Phenyl-5-phenylazo-3H-thiazol-2-ylidene)malononitrile (8a). Yield 85 %; mp 198-200 ºC; Anal. calcd. for C$_{18}$H$_{11}$N$_5$S (329.38): C, 65.64; H, 3.37; N, 21.26; S, 9.73. Found: C, 65.49; H, 3.51; S, 9.39; IR (KBr): $\nu_{max}$ = 3180 (NH), 2216 (2CN); $^{1}$H-NMR (DMSO): $\delta$, ppm = 5.03 (br, 1H, NH, D$_2$O exchangeable), 7.25-7.60 (m, 8H, Ar-H), 8.22-8.24 (m, 2H, Ar-H); $^{13}$C-NMR (DMSO): $\delta$, ppm = 175.46, 147.29, 138.67, 131.79, 131.47, 130.73 (2C), 130.70 (2C), 129.59 (2C), 128.63 (2C), 127.05, 118.96, 117.71, 115.70 (2CN). MS: $m/z$ (%) 329 (M$^{+}$, 100), 301 (20), 237 (15), 225 (25), 153 (5), 103 (20), 92 (25), 77 (65).

2-[4-(4-Chloro-phenyl)-5-phenylazo-3H-thiazol-2-ylidene]malononitrile (8b). Yield 88 %; mp 240-42 ºC; Anal. calcd. for C$_{18}$H$_{10}$ClN$_5$S (363.82): C, 59.42; H, 2.77; N, 19.25; S, 8.81. Found: C, 58.99; H, 3.02; N, 18.99; S, 8.60; IR (KBr): $\nu_{max}$ = 3183 (NH), 2222 (2CN); $^{1}$H-NMR (DMSO): $\delta$, ppm = 5.12 (br, 1H, NH, D$_2$O exchangeable), 7.25-7.60 (m, 7H, Ar-H), 8.22-8.24 (m, 2H, Ar-H); $^{13}$C-NMR (DMSO): $\delta$, ppm = 171.23, 143.49, 135.54, 132.65, 131.98, 130.56 (2C), 130.42 (2C), 128.99 (2C), 128.63 (2C), 127.83, 118.54, 117.06, 115.70 (2CN). MS: $m/z$ (%) 365 (M$^{+2}$, 40), 364 (M$^{+1}$, 20), 363 (M$^{+}$, 100), 335 (10), 259 (20), 168 (10), 137 (15), 105 (10), 92 (35), 77 (50).

2-(4-Methyl-5-phenylazo-3H-thiazol-2-ylidene)malononitrile (8c). Yield 92 %; mp 235-36 ºC; Anal. calcd. for C$_{13}$H$_{9}$N$_5$S (276.31): C, 58.41; H, 3.39; N, 26.20; S, 11.99. Found: C, 57.99; H, 3.63; N, 26.14; S, 11.59; IR (KBr): $\nu_{max}$ = 3193 (NH), 2222 (2CN); $^{1}$H-NMR (DMSO): $\delta$, ppm = 2.65 (s, 3H, CH$_3$), 4.22 (br, 1H, NH, D$_2$O exchangeable), 7.28-7.60 (m, 5H, Ar-H); $^{13}$C-NMR (DMSO): $\delta$, ppm = 169.88, 144.89, 134.44, 129.65 (2C), 129.30, 128.77 (2C), 119.77, 116.36, 114.11, 112.82 (2CN). MS: $m/z$ (%) 276 (M$^{+}$, 100), 239 (40), 176 (25), 162 (30), 98 (10), 71 (50).
General procedure for the syntheses of 9a-c
Mixtures of 7a-c (0.01 mol) and hydrazine monohydrate (0.50 g, 0.01 mol) in DMF (10 mL) were stirred at reflux for 20 h (completion assessed by TLC analysis using ethyl acetate-petroleum ether 1:1). The mixtures were cooled and poured into ice-water. The solid products, collected by filtration, were crystallized from DMF to give light yellow crystals.

4-(4-Phenylthiazol-2-yl)-1H-pyrazole-3,5-diamine (9a). Yield 78 %; mp 322-23 ºC; Anal. calcd. for C_{12}H_{11}N_{5}S (257.31): C, 56.01; H, 4.31; N, 27.22; S, 12.41. Found: C, 55.80; H, 4.41; N, 26.88; S, 11.99; IR (KBr): $\nu_{\text{max}}$ = 3372, 3256 (NH$_2$), 3176, 3112 (NH$_2$), 3132 (NH); $^1$H-NMR (DMSO): $\delta$, ppm = 5.39 (br, 4H, 2NH$_2$, D$_2$O exchangeable), 7.31-7.46 (m, 3H, Ar-H), 7.75 (s, 1H, CH), 7.96-7.98 (m, 2H, Ar-H), 10.73 (br, 1H, NH, D$_2$O exchangeable); $^{13}$C-NMR (DMSO): $\delta$, ppm = 166.29, 162.08, 152.30 (2C), 134.31, 128.69 (2C), 127.69, 125.89 (2C), 107.48, 87.97. MS: m/z (%) 257 (M$^+$, 100), 226 (10), 200 (5), 134 (35), 128 (10), 90 (10).

4-(4-(4-chlorophenyl)thiazol-2-yl)-1H-pyrazole-3,5-diamine (9b). Yield 75 %; mp 328-30 ºC; Anal. calcd. for C$_{12}$H$_{11}$ClN$_5$S (291.76): C, 49.40; H, 3.45; N, 24.00; S, 10.96. Found: C, 49.24; H, 3.61; N, 23.67; S, 10.85; IR (KBr): $\nu_{\text{max}}$ = 3369, 3289 (NH$_2$), 3248, 3176 (NH$_2$), 3123 (NH); $^1$H-NMR (DMSO): $\delta$, ppm = 5.43 (br, 4H, 2NH$_2$, D$_2$O exchangeable), 7.49 (d, 2H, Ar-H), 7.75 (s, 1H, CH), 8.00 (d, 2H, Ar-H), 10.73 (br, 1H, NH, D$_2$O exchangeable); $^{13}$C-NMR (DMSO): $\delta$, ppm = 165.79, 162.31, 151.08 (2C), 133.16, 132.09, 128.68 (2C), 127.61 (2C), 108.24, 87.94. MS: m/z (%) 293 (M$^+$, 45), 292 (M$^+$, 45), 291 (M$^+$, 100), 260 (10), 168 (35), 133 (15), 123 (5), 89 (10), 67 (5).

4-(4-Methylthiazol-2-yl)-1H-pyrazole-3,5-diamine (9c). Yield 76 %; mp 330-32 ºC; Anal. calcd. for C$_7$H$_9$N$_5$S (195.24): C, 43.06; H, 4.65; N, 35.87; S, 16.42. Found: C, 42.89; H, 4.73; N, 35.60; S, 15.98; IR (KBr): $\nu_{\text{max}}$ = 3371, 3275 (NH$_2$), 3255, 3180 (NH$_2$), 3118 (NH); $^1$H-NMR (DMSO): $\delta$, ppm = 2.23 (s, 3H, CH$_3$), 5.62 (br, 4H, 2NH$_2$, D$_2$O exchangeable), 6.86 (s, 1H, CH), 10.67 (br, 1H, NH, D$_2$O exchangeable); $^{13}$C-NMR (DMSO): $\delta$, ppm = 164.33, 161.56, 150.03 (2C), 106.88, 87.68, 16.84. MS: m/z (%) 195 (M$^+$, 100), 164 (20), 138 (10), 123 (15), 112 (5), 72 (15).

Synthesis of 4-(4-phenyl-5-phenylazo-thiazol-2-yl)-1H-pyrazole-3,5-diamine (10)
Procedure 1: A cold solution of benzenediazonium chloride (0.01 mol) was prepared by adding a solution of sodium nitrite (0.7 g into 10 mL H$_2$O) to a cold solution of aniline hydrochloride (0.93 g, 0.01 mol of aniline in 5 mL concentrated HC1) with stirring at room temperature. The resulting solution was then added to a cold solution of 9a (2.57 g, 0.01 mol) in ethanol (50 mL) containing sodium acetate (2 g). The resulting mixture was stirred for 1 h, giving a solid, which was collected by filtration and crystallized from EtOH to give the pure product as yellow crystals.

Procedure 2: A mixture of 8a (3.29 g, 0.01 mol) and hydrazine monohydrate (0.50 g, 0.01 mol) in DMF (10 mL) was stirred at reflux for 20 h (completion assessed by TLC analysis using ethyl acetate-petroleum ether 1:1 as eluent). The mixture was cooled and poured into ice-water, giving a solid that was collected by filtration and crystallized from EtOH to give the product as yellow crystals.
crystalls in a 75 % yield; mp 295-97 °C; Anal. calcd. for C_{18}H_{15}N_{7}S (361.42): C, 59.82; H, 4.18; N, 27.13; S, 8.87. Found: C, 60.10; H, 3.98; N; 27.19; S, 8.93; IR (KBr): ν_{\text{max}} = 3398, 3312 (NH_{2}), 3258, 3137 (NH_{2}); ^{1}H-NMR (DMSO): δ, ppm = 6.24 (br, 4H, D_{2}O exchangeable), 7.48-8.09 (m, 10H, Ar-H). MS: m/z (%) 361 (M^+, 100), 340 (60), 323 (15), 224 (45), 136 (40), 124 (10), 90 (15).

**Synthesis of 2-(2-phenylthiazolo[5,4-c]pyridazin-6(2H)-ylidene)malononitrile (12)**

A mixture of 8c (2.76 g, 0.01 mol) and N,N-dimethylformamide dimethyl acetal (DMFDMA, 1.19 g, 0.01 mol) in DMF (10 mL) was stirred at reflux for 14 h. Concentration the mixture in vacuo gave a residue which was crystallized from EtOH to give the product as dark yellow crystalls in a 75 % yield; mp 298-299 °C; Anal. calcd. for C_{14}H_{7}N_{5}S (277.30): C, 60.64; H, 2.54; N, 25.26; S, 11.56. Found: C, 60.39; H, 2.66; N; 25.19; S, 11.23; IR (KBr): ν_{\text{max}} = 2192 (2CN); ^{1}H-NMR (DMSO): δ, ppm = 7.34-7.50 (m, 6H, Ar-H, CH), 7.65 (d, 1H, J = 5, CH). MS: m/z (%) 277 (M^+, 100), 256 (10), 169 (15), 129 (10), 93 (15), 77 (60), 73 (20).

**Synthesis of 3-(4-Methyl-thiazol-2-yl)-7-phenyl-pyrazolo[1,5-a]pyrimidin-2-ylamine (14)**

A mixture of 9c (1.95 g, 0.01 mol) and 3-dimethylamino-1-phenyl-propenone 13 (1.75 g, 0.01 mol) in DMF (10 mL) was stirred at reflux for 10 h (completion assessed by TLC analysis using ethyl acetate-petroleum ether 1:1 as eluent). The reaction mixture was cooled and poured into ice-water giving a solid which was collected by filtration and crystallized from DMF to give a the product as yellow crystals in a yield of 80 %; mp 285-87 °C; Anal. calcd. for C_{16}H_{13}N_{5}S (307.37): C, 62.52; H, 4.26; N, 22.78; S, 10.43. Found: C, 62.35; H, 4.39; N; 22.72; S, 10.18; IR (KBr): ν_{\text{max}} = 3380, 3279 (NH_{2}); ^{1}H-NMR (DMSO): δ, ppm = 2.41 (s, 3H, CH_{3}), 6.88 (br, 2H, NH_{2}, D_{2}O exchangeable), 7.13 (d, 1H, J = 5.4, CH), 7.60-8.10 (m, 5H, Ar-H), 8.56 (d, 1H, J = 5, CH); ^{13}C-NMR (DMSO): δ, ppm = 195.12, 158.00, 150.33, 149.45, 146.80, 144.65, 130.93, 130.64, 129.39 (2C), 128.41 (2C), 110.30, 106.78, 89.28, 16.79. MS: m/z (%) 307 (M^+, 100), 234 (15), 182 (5), 156 (15), 103 (5), 72 (30).

**Acknowledgements**

The authors are grateful to Kuwait University Research Administration for financial support of project SC 01/10. Financial support to Mr. Moustafa Sherief by the College of Graduate Studies is highly appreciated. The use of analytical facilities provided by SAF projects No. GS 01/05 & GS 03/01 are greatly appreciated.
References

11. CCDC 771782 contains the supplementary crystallographic data for compound 14. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk).