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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF *N*-BROMOBENZOYL-*N*'-(1,10-PHENANTHROLIN-5-YL)THIOUREA DERIVATIVES

(Sintesis dan Penentuan Struktur Ligan Terbitan *N*-Bromobenzoil-*N*'-(1,10-Fenantrolin-5-il) tiourea)

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Abstract

Derivatives of *N*-bromobenzoyl-*N*'-(1,10-phenanthrolin-5-yl)thiourea were successfully synthesized from the reaction of 1,10-phenanthroline with *x*-bromobenzoylisothiocyanate (*x* = *ortho*, *meta* and *para*) to give phen-*o*-BrBT, phen-*m*-BrBT and phen-*p*-BrBT, respectively. The molecular structures of the derivatives compounds were elucidated based on the crystal structure of *N*-bromobenzoyl-*N*'-(1,10-phenanthrolin-5-yl)thiourea, CHNS elemental analysis, mass spectrometry, spectroscopic data (infrared, ultraviolet-visible, nuclear magnetic resonance and luminescence) and cyclic voltammetry.The mass spectrum show similar *m/z* values at 460.9 and 260.0, which represent the molecular ions for $[(phen\text{-}x\text{-}BrBT)\text{-}Na]^+$ and $[BrBT]^+$, respectively. The presence of a ν(NH) (3389-3599 cm^{-1}) and the disappearance of $\nu(NH_2)$ bands from 1,10-phenanthroline-5-amine indicate the formation of the *N*-bromobenzoyl-*N*'-(1,10-phenanthrolin-5-yl)thiourea. Attachment of a Br atom to the benzoyl moiety reduced the stretching frequency of C=O group by >20 cm^{-1} compared with phen-BT ligand. The compounds exhibit two $\pi\rightarrow\pi^*$ bands at 231 and 269-270 nm for the phenanthroline and benzoyl moieties, respectively. The resonance for N-H proton appeared at δ = 11.53-12.49 ppm. In addition, ^{13}C resonance signals for C=S and C=O groups were recorded at around 182 and 167.39-169.08 ppm, respectively. The synthesis and effect of a Br substitution on the structural and luminescence properties of *N*-bromobenzoyl-*N*'-(1,10-phenanthrolin-5-yl)thiourea derivatives are presented and discussed in this study.

Keywords: benzoylthiourea, 1,10-phenanthroline, thiocyanate, infrared, luminescence

Abstrak

Terbitan *N*-bromobenzoil-*N*'-(1,10-fenantrolin-5-il)tiourea telah disintesis melalui tindak balas di antara 1,10-fenantrolina dengan *x*-bromobenzoilisotiosianat (*x* = *orto*, *meta* and *para*) masing-masing menghasilkan sebatian phen-*o*-BrBT, phen-*m*-BrBT dan phen-*p*-BrBT. Struktur sebatian ditentukan berdasarkan struktur kristal *N*-benzoil-*N*'-(1,10-fenantrolin-5-il)tiourea, analisis unsur CHNS, spektrometri jisim, data spektroskopi (inframerah, ultralembayung-boleh nampak, pendarcahaya dan resonans magnetik nuklear) dan voltammetry kitaran. Spektrum jisim bagi ketiga-tiga sebatian ini menunjukkan nilai *m/z* yang sama pada 460.9 dan 260.0 masing-masing mewakili ion molekul $[(phen\text{-}x\text{-}BrBT)\text{-}Na]^+$ dan $[BrBT]^+$. Kemunculan isyarat ν(NH) pada 3389-3599 cm^{-1} dan kehilangan frekuensi regangan $\nu(NH_2)$ bagi sebatian 1,10-fenantrolin-5-amina menunjukkan pembentukan molekul *N*-bromobenzoil-*N*'-(1,10-fenantrolin-5-il)tiourea. Kehadiran atom bromo pada gelang benzoil telah merendahkan frekuensi regangan ν(CO) sebanyak >20 cm^{-1} berbanding *N*-bromobenzoil-*N*'-(1,10-fenantrolin-5-il)tiourea. Spektrum elektronik sebatian memapar dua jalur serapan bagi peralihan $\pi\rightarrow\pi^*$ pada 231 dan 269-270 nm masing-masing berpunca daripada moieti fenantrolina dan benzoil. Isyarat resonan ^1H (N-H) hadir pada δ = 11.53-12.49 ppm manakala, isyarat ^{13}C bagi kumpulan berfungsi utama C=S dan C=O telah dikenal pasti masing-masing pada 182 dan 167.39-169.08 ppm. Sintesis dan kesan

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kehadiran Br pada posisi *orto*, *meta* dan *para* terhadap struktur serta sifat pendarcahaya sebatian dilapor dan dibincang di dalam kajian ini.

Kata kunci: benzoilthiourea, 1,10-fenantrolina, tiosianat, inframerah, pendarcahaya

Introduction

Polypyridine compounds such as 1,10-phenanthroline (phen) are one of the most widely used chelating ligands in modern coordination chemistry [1,2]. The shape of the phen favors the formation of metal complexes via chelation and hence, phen and its derivatives are widely used ligands in metal complexes. The metal complexes of phen derivatives have many applications in various fields such as molecular catalysis, solar energy conversion, herbicides and nucleic acid probes. Besides, metal-phen compound has also been used in the development of luminescence-based sensors for pH, anions and cations [3].

Thiourea compounds are essential as building blocks in the synthesis of heterocyclic compounds [4]. Substituted thioureas have gained great attention in the preparation of wide variety of biologically active compounds [5,6]. Thioureas are also an important class of organic compounds, which showed high biological activity, used as corrosion inhibitors and antioxidant, and were also widely used as polymer components [7]. The synthesis of thiourea derivatives can be easily done with a good yield [8]. One of the thiourea derivatives that have gained a lot of attention is benzoylthiourea, which has shown a wide range of biological activities including antiviral [9], antibacterial [10,11], antifungal [12], herbicidal [13] and acting as chelating agents [14,15].

Phenanthroline derivatives and bromobenzoylthiourea compounds are widely used chelating agents in the coordination chemistry [1,4]. This study attempts to combine both classes of the compounds to form a multi-dentate benzoylthiourea ligand that contains both moieties. Subsequently, this new multi-dentate chelating ligand can be used to form stable complexes with metal ions. The derivatives of *N*-bromobenzoyl-*N*'-(1,10-phenanthrolin-5-yl)thiourea compounds are expected to be a more effective class of the organic compounds to coordinate with metal ions due to the presence of lone pair electrons on nitrogen, sulphur and oxygen atoms. In addition, the π-electron cloud in the phen and benzoylthiourea moieties will also add to the stability of the coordination complexes through delocalization of electrons across the coordination sphere.

In this paper, we present the synthetic method, structural and electronic properties of *N*-bromobenzoyl-*N*'-(1,10-phenanthrolin-5-yl)thiourea derivatives. In addition we also discussed the effects of the Br substitution on the structural and luminescence properties of the compounds.

Materials and Methods

Chemicals and instrumentation

Benzoyl chloride, 1,10-phenanthroline-5-amine, *o*-bromobenzoyl chloride, *m*-bromobenzoyl chloride and *p*-bromobenzoyl chloride were purchased from Fluka (Malaysia). All solvents were of reagent grade quality and were obtained from commercial suppliers and used without further purification.

Melting points were determined on an Electrothermal 9100. Elemental (C, H, N and S) analyses were performed on Leco 932 analyzer. The mass spectra were recorded on a Bruker micrOTOF-Q 86 spectrometer equipped with an electrospray ionization (ESI) module. The source temperature was maintained at 180 ˚C at an approximately 0.4 bar pressure. Infrared measurements of the complexes were recorded by using Agilent Cary 630 spectrophotometer in the range of 4000-400 cm^{-1} in the ATR Diamond mode, whereas the UV-Vis absorption spectra were obtained by using a 1 cm path length quartz cell on a Perkin-Elmer Lambda 35 spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were collected on a ECP 400 (Delta-NMR) spectrophotometer as deuterated DMSO solution. The chemical shifts were scaled to parts per million (ppm) with reference to TMS. The electrochemical measurements were carried out with a Voltalab PGZ402, AmetekVersastat 4 system. Steady state emission spectra were recorded on an Edinburgh FLS920 time resolved fluorescence spectrometer at 298 K in CH_3CN, using 1 cm path length quartz cell.

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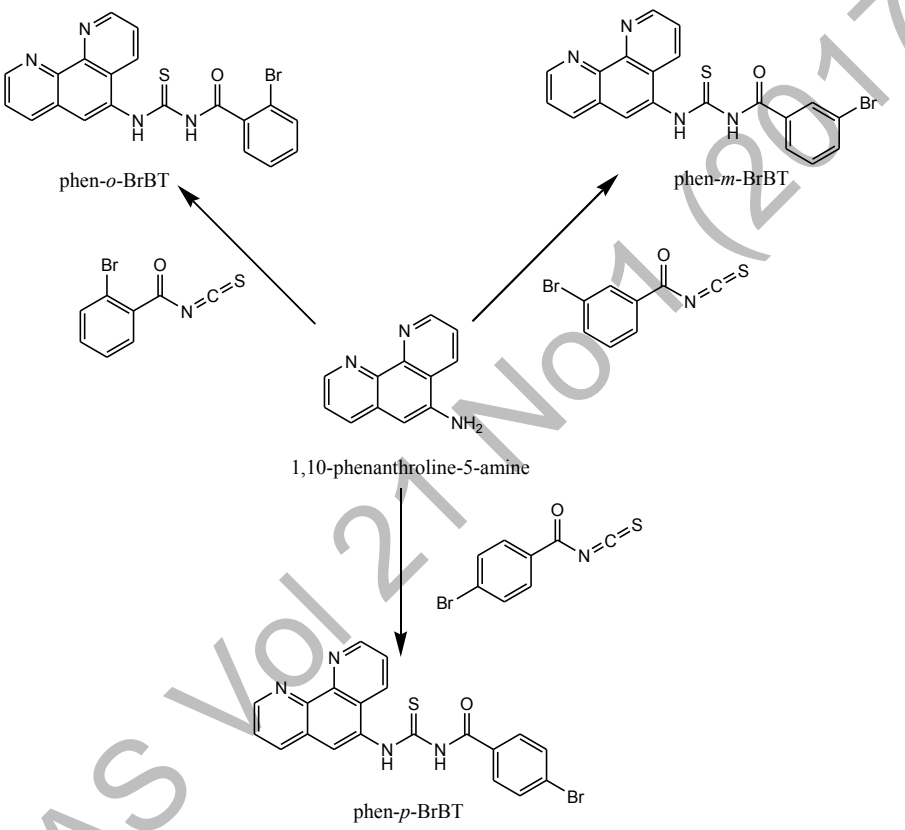
Synthesis of *N*-(x-bromobenzoyl)-*N*'-(1,10-phenanthrolin-5-yl)thiourea

Firstly, *ortho*-, *meta*- and *para*-bromobenzoyl chloride derivatives (1.5 mmol) were reacted with ammonium thiocyanate (1.15 mmol) in acetone (30 ml) to give the corresponding bromobenzoylisothiocyanate derivatives followed by a condensation with 1,10-phenanthroline-5-amine in ethanol (20 ml) to give *o*-bromobenzoyl-(1,10-phenanthrolin-5-yl)thiourea [phen-*o*-BrBT], *m*-bromobenzoyl-(1,10-phenanthrolin-5-yl)thiourea [phen-*m*-BrBT] and *p*-bromobenzoyl-(1,10-phenanthrolin-5-yl)thiourea [phen-*p*-BrBT] compounds, respectively (Scheme 1). The reaction mixtures were left to stir for 5 hours at 80˚C. The products were collected as yellow precipitates and the solvents were removed under reduced pressure. The precipitates were then rinsed with cold acetone to give the desired products. Recrystallization in a suitable solvent gave a pure yellowish crystalline product.



Scheme 1. Schematic diagram for the synthesis of *N*-(*x*-bromobenzoyl)-*N*'-(1,10-phenanthrolin-5-yl)thiourea derivatives from *x*-bromobenzoylisothiocyanate and 1,10-phenanthroline-5-amine

Results and Discussion

The phen-BT, phen-*o*-BrBT, phen-*m*-BrBT and phen-*p*-BrBT compounds were characterized on the basis of the mass spectrometry, CHNS elemental analysis and the spectroscopic data from infrared, ultraviolet-visible, nuclear magnetic resonance (^{1}H and ^{13}C) spectroscopy. Besides, the cyclic voltammetry and luminescence properties of these compounds also were recorded to provide more information on the electronic states and structures. Overall, the reactions gave a reasonable to good yield (58-68%) as summarized in Table 1.

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Table 1. The yield and melting point of *N*-(bromobenzoyl)-*N*'-(1,10-phenanthrolin-5-yl)thiourea derivatives

Compound	Yield (%)	Melting point (°C)
phen-BT	65.0	-
phen-*o*-BrBT	63.5	197.5 – 198.3
phen-*m*-BrBT	57.9	146.3 – 151.3
phen-*p*-BrBT	68.0	175.2 – 176.5

Elemental analysis of C, H, N and S

There was some deviation from the theoretical value for C, H, N and S contents in the phen-BT, phen-*o*-BrBT, phen-*m*-BrBT and phen-*p*-BrBT compounds. These differences are within the experimental errors and may be due to a contamination from the recrystallization solvent and atmospheric water. This is not uncommon as the solvent is quite polar and the compound contains Br atom that can also induce polarity in the molecule. We proposed a new chemical formula for each compound taking into consideration that the samples might be contaminated as shown in Table 2. The calculation revealed that the highest deviation (0.86) was for carbon content in the phen-*p*-BrBT sample.

Table 2. The elemental CHNS contents in phen-BT, phen-*o*-BrBT, phen-*m*-BrBT and phen-*p*-BrBT and the proposed new chemical formula to account for an acetone and water content

Compound	Experiment (theory), %				Proposed Chemical Formula	Largest Deviation (Element)
	C	H	N	S		
phen-BT	66.61 (67.02)	4.83 (3.94)	15.78 (15.63)	8.73 (8.95)	$C_{20}H_{14}N_4OS \cdot 0.2H_2O \cdot 0.15C_3H_6O$	0.67 (H)
phen-*o*-BrBT	53.54 (54.93)	4.47 (3.00)	11.72 (12.81)	7.22 (7.33)	$C_{20}H_{13}BrN_4OS \cdot 1.1H2O \cdot 0.55 C_3H_6O$	0.66 (H)
phen-*m*-BrBT	53.59 (54.93)	4.12 (3.00)	12.03 (12.81)	7.17 (7.33)	$C_{20}H_{13}BrN_4OS \cdot 0.95H_2O \cdot 0.4C_3H_6O$	0.47 (H)
phen-*p*-BrBT	56.55 (54.93)	4.05 (3.00)	12.14 (12.81)	7.37 (7.33)	$C_{20}H_{13}BrN_4OS \cdot 0.9C_3H_6O$	0.86 (C)

Mass spectrometry

The electron impact mass-spectrum of a representative compound namely phen-*p*-BrBT (Figure 1) shows the corresponding *m/z* value of the parent molecule with one mole of associated sodium ion, $[\text{phen-}x\text{-BrBT})\text{-Na}]^+$ at 460.9 (459.0 *theory*). A fragmentation with *m/z* value corresponding to $[\text{BrBT}]^+$ was observed at 260.0 (258.9 *theory*). Similarly, the mass spectrum and the fragmentation masses of other derivatives agreed with the structures as shown in Figure 1.

X-ray crystal structures

The structure of *N*-(benzoyl)-*N*'-(1,10-phenanthrolin-5-yl)thiourea [phen-BT] [16] (Figure 2) was used as a reference to provide additional information in the determination of the molecular structure of the bromo-substituted analogues.

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Formula

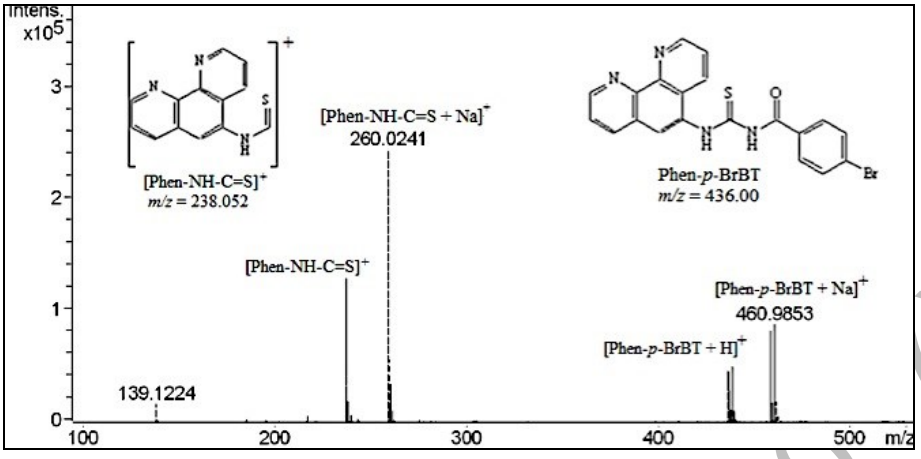

Figure 1. ~~The GC-MS spectrum for the representative phen-*p*-BrBT compound~~

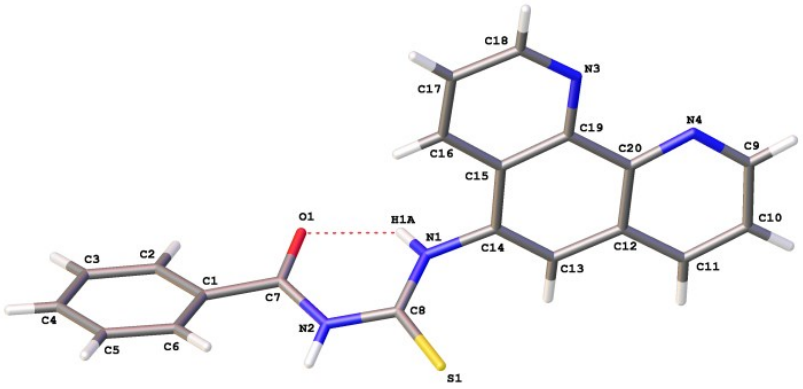

Figure 2. The molecular structure of the phen-BT with a dashed line indicates the intramolecular hydrogen bond that forms a pseudo-six membered ring

In the structure of phen-BT, the benzoyl and 1,10-phenanthroline moieties were attached to the terminal nitrogen atoms of the thiourea moiety at *cisoid* and *transoid* position relative to the thiono N2—C8 and N1—C8 bonds. The phenyl and phenanthroline rings are twisted relative to the central thiourea fragment with dihedral angles of 29.46(12)˚ and 74.06(8)˚, respectively. The phenyl and phenanthroline rings are almost perpendicular to each other with dihedral angle of 83.15(10)˚.

The S1—C8 and O1—C7 in the compound showed a typical double bond character with bond lengths of 1.651(2) and 1.222(3) Å respectively, and are comparable to other thiourea derivatives [17,18]. All C-N bonds (N2—C7, N2—C8, N1—C8 and N2—C14) in the thiourea fragments were in the range of 1.431(3) to 1.329(3) Å, which are an intermediate distance between those expected for single and double CN bonds (1.47 and 1.27 Å, respectively). Among these CN bonds, we noticed that N2—C14 was the longest bond, which indicated a C_{sp^2}-N_{sp^2} single bond while N1—C8 bond was the shortest bond with more double bond character.

In the crystal structure of phen-BT compound, there was an intramolecular hydrogen bond, N1—H1A···O1 resulting in the formation of a pseudo six-membered ring (N1/H1A/O1/C7/N2/C8) in the molecule. The present of the intramolecular hydrogen bond may contributed to the shift in the infrared signal of the C=O group and to a lesser extend to the ^{1}H and ^{13}C signals of the compounds since the spectrum were collected in a solution phase.

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The mass-spectrum showing the molecular ion of phen-*p*-BrBT and its fragmentations as a representative compound.

Infrared spectra

The infrared spectrum of phen-BT is shown in Figure 3 and the characteristic functional groups are listed in Table 3. Generally, the IR spectrum of 1,10-phenanthroline moiety shows strong bands in the 1400-1650 cm^{-1} regions [19]. A band at around 1420 cm^{-1} exhibits the stretching frequency of $\nu(C\text{-}N_{phen})$, which indicates a highly delocalized electronic distribution in the thiourea moiety.

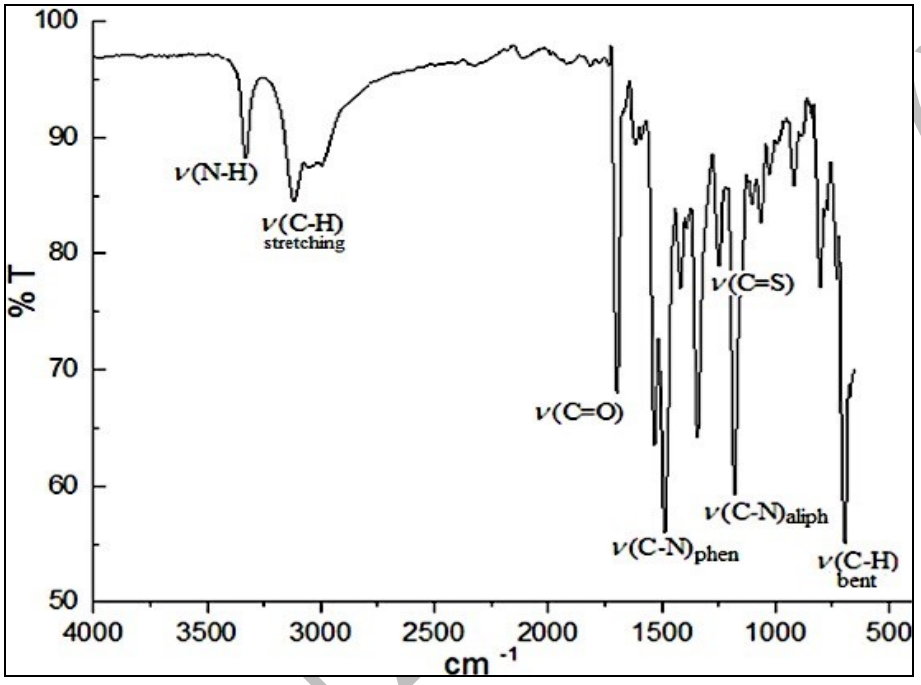

Figure 3. The Infrared spectrum of phen-BT

Table 3. The stretching frequencies of characteristic functional groups for phen-BT, phen-*o*-BrBT, phen-*m*-BrBT and phen-*p*-BrBT compounds

Compound	IR spectrum (cm^{-1})			
	ν(NH)	$\nu(C\text{-}N_{phen})$	ν(C=O)	ν(C=S)
phen-BT	3332	1420	1700	1254
phen-*o*-BrBT	3513	1422	1672	1258
phen-*m*-BrBT	3513	1422	1673	1251
phen-*p*-BrBT	3596	1420	1676	1259

It is important to note the disappearance of $\nu(NH_2)$ stretching frequency of the amine group and the appearance of ν(NH) stretching band at 3332, 3513, 3513 and 3596 cm^{-1} in the spectra of phen-BT, phen-*o*-BrBT, phen-*m*-BrBT and phen-*p*-BrBT, respectively. The later band is an important indicator for the formation of the *N*-bromobenzoyl-*N*'-(1,10-phenanthrolin-5-yl)thiourea molecules. In addition, bands at 3521-3599 cm^{-1} regions indicate the asymmetric and symmetric vibrations frequencies for (N-H) of the secondary thioamide group.

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infrared

A strong band at 1672-1700 cm^{-1} was ascribed to the stretching vibration of the C=O group. The wavelength for the C=O band decreases by >20 cm^{-1} due to a more delocalised electronic distribution across the structural geometry and the presence of an intramolecular hydrogen bonding between the O atom of the C=O group with N-H as suggested by the X-ray crystal structure [20]. Furthermore, the presence of bromo atom as an electron-withdrawing group at the benzoyl moiety has weakened the C=O bond. Halogen atom with high electronegativity such as bromine is capable of reducing the electron density of the benzene ring and hence, has indirectly affected the neighbouring C=O group.

Ultraviolet-visible spectra

The UV absorption spectra of the phen-BT, phen-*o*-BrBT, phen-*m*-BrBT and phen-*p*-BrBT compounds are shown in Figure 4 and the data is collected in Table 4. The ligands display two strong absorption bands in the ultra-violent region with absorption maxima at 231 (ε= 54,795-61,870 $Lmol^{-1}cm^{-1}$) and 269-270 nm (ε= 36,711-57,513 $Lmol^{-1}cm^{-1}$) that can be attributed to the π→π* ligand-centred (LC) transitions.

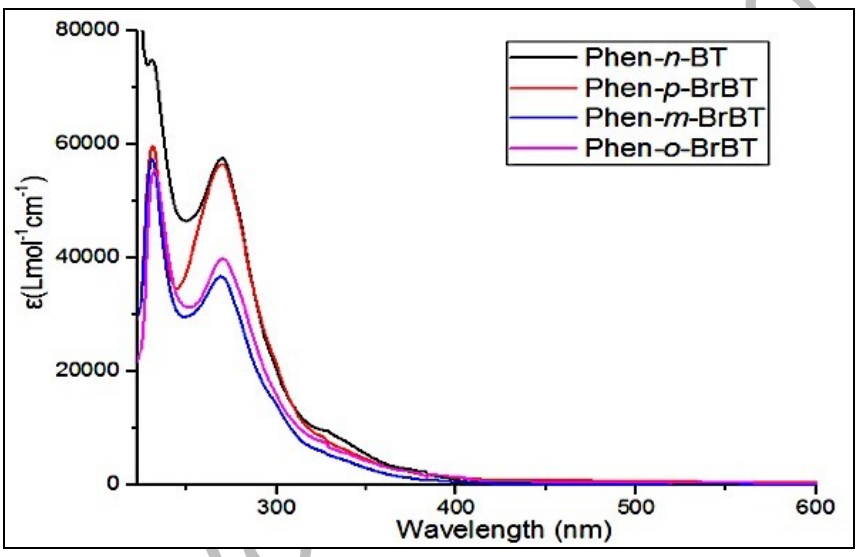

Figure 4. The electronic absorption spectra of *N*-bromobenzoyl-*N'*-(1,10-phenanthrolin-5-yl)thiourea derivatives in acetonitrile

The intensity of phen-*p*-BrBT absorption band appears the highest compared to phen-*m*-BrBT and phen-*o*-BrBT. In addition, there is no significant change in the energy of the electronic absorption bands compared with the substituted phen-BT. However, the bromo-substituent in the phen-*o*-BrBT molecule has a restricted structural conformation and appeared to impede the electron transfer slightly for the higher energy transitions.

Table 4. Molar absorptivity and λ_{max} of phen-BT, phen-*o*-BrBT, phen-*m*-BrBT and phen-*p*-BrBT compounds

Compound	**UV-Vis (CH_2Cl_2)**
	λ(nm) / ε($Lmol^{-1}cm^{-1}$)
phen-BT	270 (57,513), 231 (61,870)
phen-*o*-BrBT	269 (39,828), 231 (54,795)
phen-*m*-BrBT	269 (36,711), 231 (57,405)
phen-*p*-BrBT	270 (56,517) , 231 (59,724)

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frequency

Nuclear magnetic resonance spectroscopy

The structures of all compounds with the atomic numbering scheme are shown in Figure 5. The data are compiled in Table 5 and Table 6, respectively. In accordance with the IR spectra, the chemical shift of $H(N_1)$ were observed at 12.36, 12.49 and 12.53 ppm for phen-*o*-BrBT, phen-*m*-BrBT and phen-*p*-BrBT, respectively. The signal for the amine proton $\delta H(N_1)$ appears as the most deshielded proton signals since the proton was influenced by two electronegative groups (C=O and C=S) in the proximate distances. The signals of $\delta H(N_2)$ were slightly shielded and were observed in the downfield region at 12.26, 12.01 and 11.97 ppm for phen-*o*-BrBT, phen-*m*-BrBT and phen-*p*-BrBT, respectively. The signals for the phenanthroline protons were observed in the downfield region at δ=7.46-9.15 ppm.

Table 5. The ^{1}H NMR signals of the *N*-(bromobenzoyl)-*N'*-(1,10-phenanthrolin-5-yl)thiourea derivatives

Proton	**δ, ppm (coupling patterns, *J-coupling*, proton)**			
	Phen-BT	**Phen-*o*-BrBT**	**Phen-*m*-BrBT**	**Phen-*p*-BrBT**
HNa	12.63 (s,H)	12.36 (s, H)	12.49 (s,1H)	12.53 (s,1H)
HNb	11.88 (s,1H)	12.26 (s,1H)	12.49 (s,1H)	12.53 (s,1H)
H9, H16	12.53 (s,1H)	9.14 (m, J_1=3.9 Hz, J_2=1.6 Hz,2H)	9.13 (t, J= 4.2 Hz,2H)	9.13 (t, J_1= 4.9 Hz,2H)
H12	8.20 (s,1H)	8.18 (s,1H)	8.25 (s,1H)	8.16 (s,1H)
H10, H15	8.08 (m, J_1= 7.6 Hz, 2H)	7.83 (m, J_1= 19.9 Hz, J_2= 4.1 Hz, 2H)	7.82 (m, J_1= 8.4, J_2= 4.3 Hz, 2H)	7.99 (m, J_1= 8.1 Hz, 2H)
H11, H14	8.52 (dd, J_1= 18.7 Hz, J_2= 8.2 Hz, 2H)	8.55 (dd, J_1= 8.1 Hz, J_2= 1.5 Hz, 1H) 8.43 (dd, J1= 8.2 Hz, J2= 1.3 Hz, 1H)	8.54 (d, J_1= 8.1 Hz,1H) 8.49 (d, J_1= 8.4 Hz,1H)	8.53 (d, J= 8.1 Hz,1H) 8.48 (d, J1= 8.4 Hz,1H)
Phenyl ring (H2,H3,H4,H5,H6)	7.87-7.78 (m, 2H)/$\delta_{H2\&H6}$ 7.70(t, J_1= 7.3 Hz, 1H)/δ_{H4} 7.59 (t, J_1= 7.7 Hz, 2H)/$\delta_{H3\&H5}$	7.76 (d, J1=8.1 Hz, 1H)/δ_{H2} 7.71 (d, J1= 6.2 Hz, 1H)/δ_{H6} 7.58-7.45 (m, 2H)/$\delta_{H4\&H5}$	8.16 (s,1H)/δ_{H2} 8.16 (s,1H)/δ_{H2} 7.54 (t, J_1= 7.9Hz, 1H)/δ_{H5} 7.88 (d, J_1= 8.1 Hz, 1H) δ_{H4}	7.85-7.77 (m,4H)/$\delta_{H2,H3,H5\&H6}$

s: singlet; d: doublet; t: triplet; m: multiplet

Table 6. The ^{13}C NMR signals of the *N*-(bromobenzoyl)-*N'*-(1,10-phenanthrolin-5-yl)thiourea derivatives

Carbon	**δ, ppm**			
	Phen-BT	**Phen-*o*-BrBT**	**Phen-*m*-BrBT**	**Phen-*p*-BrBT**
C=S	182.49	182.04	182.39	182.43
C=O	168.75	169.08	167.39	167.98
C9, C16	132.97	146.42	146.38	146.45
	132.69	145.43	145.36	145.43

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Table 6 (cont'd). The ^{13}C NMR signals of the *N*-(bromobenzoyl)-*N*'-(1,10-phenanthrolin-5-yl)thiourea derivatives

Carbon	δ, ppm			
	Phen-BT	**Phen-*o*-BrBT**	**Phen-*m*-BrBT**	**Phen-*p*-BrBT**
C10, C15	125.37	128.34	128.46	125.43
		128.18	128.33	126.23
C11	137.37	133.68	136.27	132.60
C12	126.32	129.86	125.46	127.72
C14	128.39	133.24	132.67	131.46
C17, C20	150.54	150.90	150.87	150.88
	150.48	150.66	150.66	150.66
C18, C19	129.33	132.76	126.24	128.32
	128.99	132.46		
C1, C13	133.85	137.12	125.05	132.08
	133.71	136.95	133.77	132.00
C2	124.01	126.23	124.22	123.84
C3	124.29	125.57	136.97	124.19
C4	123.77	125.57	123.86	133.75
C5	124.29	123.88	131.23	123.19
C6	124.01	119.44	122.07	123.84

As for the ^{13}C NMR spectra, the most downfield signals were attributed to the resonances of C=S and C=O groups. The carbon atoms of the thiocarbonyl group appeared at 182.04, 182.39 and 182.04 ppm for phen-*o*-BrBT, phen-*m*-BrBT and phen-*p*-BrBT, respectively. The results revealed that the C=S signal was shifted downfield compared to that of C=O (167.39-169.08 ppm), which is partly due to the resonance effects of the CO and -NH- groups. These features and chemical shifts of the ^{1}H and ^{13}C NMR spectra are in agreement with the crystal structure of phen-BT as depicted in Figure 5.

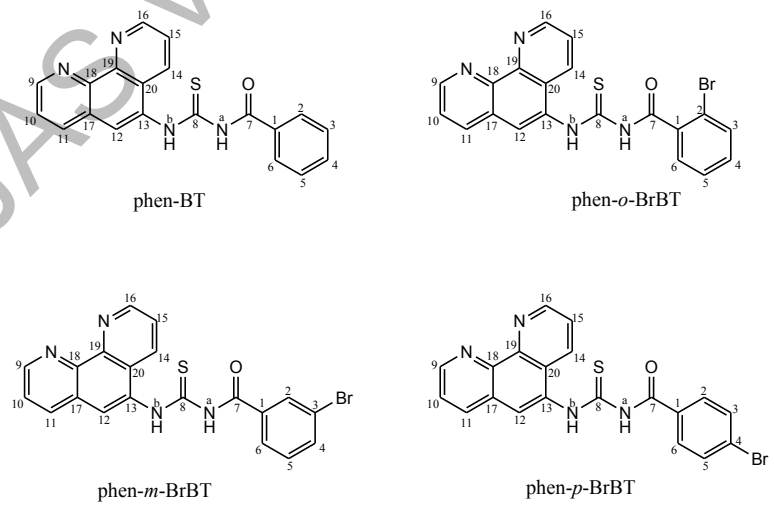

Figure 5. The structure of *N*-(bromobenzoyl)-*N*'-(1,10-phenanthrolin-5-yl)thiourea derivatives with the atomic numbering scheme for NMR structure elucidation

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Cyclic voltammetry

Cyclic voltammetry is an important technique in electrochemistry analysis because it provides useful information on electron transfer process. The electrochemical cell consist of three electrodes - a platinum disk working electrode (2 mm, diameter), Ag/Ag^+ reference electrode (0.01 M $AgNO_3$; 0.1 M tetrabutylammonium perchlorate in CH_2Cl_2) and a platinum counter electrode. The potentials (1 mM) were recorded in CH_2Cl_2 with 0.1 M $[(n\text{-}C_4H_9)_4N]PF_6$. All compounds exhibit an irreversible oxidation and reduction redox couples. The redox potentials are listed in Table 7.

Table 7. The redox potentials for oxidation and reduction processes of phen-BT, phen-*o*-BrBT, phen-*m*-BrBT and phen-*p*-BrBT

Compound	Irreversible processes	
	E_p^{ox}	E_p^{red}
Phen-BT	+1.68	-1.43
Phen-*o*-BrBT	+1.70	-1.50
Phen-*m*-BrBT	+1.42	-1.60
Phen-*p*-BrBT	+1.60	-1.21

All derivatives showed irreversible redox potentials at (1.42 – 1.70) V and –(1.21 – 1.60) V for oxidation and reduction processes, respectively. Bromine atom has an overall destabilizing influence on the phenyl ring with the *o*- and *p*-bromo substituents exert higher stabilization to the phenyl ring. Thus, phen-*m*-BrBT was relatively easier to be oxidized compared with the phen-*o*-BrBT and phen-*p*-BrBT derivatives. Likewise, phen-*o*-BrBT and phen-*p*-BrBT derivatives would be much easier to be reduced, i.e. accept electron. However, only phen-*p*-BrBT derivative behaves as expected. Other factors such as solvent interactions might influence the redox behaviours of the molecules.

Luminescence properties

The concentration of the compounds is 9 x 10^{-6} mol dm^{-3} and the luminescence quantum yields were calculated by using 2-aminopyridine ligand as a standard with ϕ_{std}= 0.37 in CH_3CH_2OH [19]. Figure 6 shows the emission spectra of the compounds. The excitation wavelength (λ_{ex}) for each sample was selected according to their absorption wavelength (λ_{max}) and listed in Table 8. Phen-*m*-BrBT, shows a relatively high fluorescence quantum yield (ϕ_s = 5.40 x 10^{-2} s) compared with that of *para* and *ortho* substituted analogues.

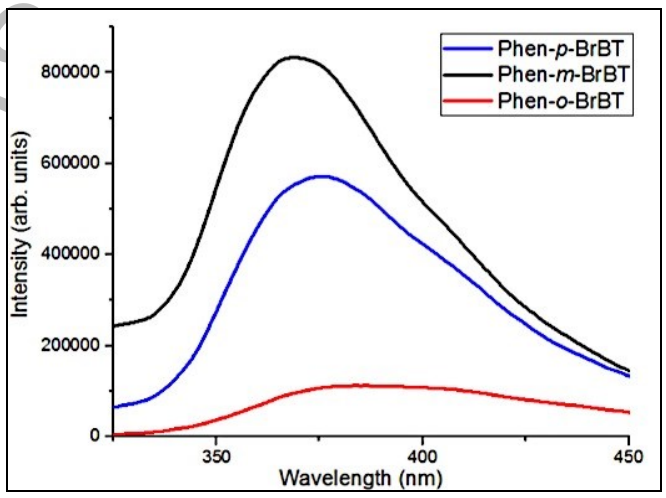

Figure 6. The steady-state fluorescence spectra of Br-substituted Phen-BT compounds measured in CH_2Cl_2

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Table 8. The emission spectra, λ_{em} of phen-BT, phen-*o*-BrBT, phen-*m*-BrBT and phen-*p*-BrBT compounds

Ligands	λ_{ex} **(nm)**	λ_{em} **(nm)**	**Quantum Yield,** φ_s **in** CH_2Cl_2
Phen-BT	270	365	7.27×10^{-2}
Phen-*o*-BrBT	269	379	5.61×10^{-3}
Phen-*m*-BrBT	269	369	5.40×10^{-2}
Phen-*p*-BrBT	270	375	2.29×10^{-2}

Conclusion

The phen-*o*-BrBT, phen-*m*-BrBTand phen-*p*-BrBT compounds were successfully synthesized and characterized by analytical and spectroscopic techniques. The molecular structural properties are in agreement with the previously reported phen-BT crystal structure. The bromo atom at the *orto*, *meta* and *para* positions of the phenyl ring in the benzoyl moiety has weakened the C=O bond by reducing the electron density of the phenyl ring. In addition, the luminescence quantum yield appears to the affected by the Br substituent with the phen-*m*-BrBT derivative showing the highest quantum yield.

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