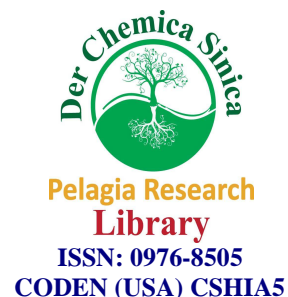




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Der Chemica Sinica, 2013, 4(1):24-31



### Green chemical synthesis and photochemical reactions of symmetrical phthalic bis-amine dithiocarbamic anhydrides

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#### ABSTRACT

*A rapid, efficient, clean and environmentally benign exclusive method of synthesis of symmetrical phthalic bis-amine dithiocarbamic anhydrides has been developed using reaction of sym-phthaloyl dichloride with amine dithiocarbamic anhydride effectively in an aqueous medium with excellent yields under microwave irradiation. The results were compared with conventional methods. All the ecofriendly synthesized symmetrical phthalic bis-amine dithiocarbamic anhydrides were characterized by analytical and spectral methods. The photochemical decomposition of symmetrical phthalic bis-amine dithiocarbamic anhydrides yielded a mixture of several products, consisting of trans-biphtalyl and amine thiuram disulfide as major products. The mechanisms of the green synthesis and photochemical reactions have also been studied.*

**Keywords:** Green synthesis, microwave irradiation, photochemical reactions, symmetrical phthalic bis-amine dithiocarbamic anhydrides

#### INTRODUCTION

The organic synthesis is one of the major role of research in chemistry, from plastics to medication it participates in the improvements of everyone life. Over the past few decades, many significant advances in practical aspects of organic chemistry have included novel synthetic strategies and methods as well as advent of a vast array of analytical techniques. In these environmentally conscious days, the developments in the technology are directed towards environmentally sound and cleaner procedures. Hence, the present day chemists are no longer confined to using only thermal energy for driving chemical reactions. With increasing complexity of the problems and the availability of newer methods of activation of chemical reactions, chemist have restored to using wide variety of techniques such as photochemical, electrochemical, sonochemical, microwave and enzymatic methods. With easy availability of ultrasound and microwave sources, their use in chemistry has gained momentum recently.

Green chemistry [1-5] revolves around the design, development and implementation of chemical processes and products that reduce or eliminate hazardous substances in a way i.e. feasible and economically viable. That is why it is placed in the frontier areas of chemical research and has been focused for considerable recent research. It is a more eco-friendly green alternative to conventional chemistry practices. It applies not only to the manufacture and use of chemical products- solvents, raw materials and intermediates, but also to the manufacture and use of pharmaceutical and biotech products, consumer and household products and to just about any imaginable article of manufacture or manufacturing process one can name. The chemical and pharmaceutical industries are always under pressure to develop more environmentally friendly organic reaction methodologies. Microwave irradiation, has been

shown not only to reduce reaction times but often to provide higher yields of the desired products as compared to traditional heating methods [6-7]. Therefore, microwave irradiation is used for a variety of organic reactions due to its use in more rapid and cleaner syntheses of organic compounds. All thermally driven reaction can be accelerated by microwave. The spectacular results *viz.* shorter reaction time, experimental simplicity selectivity of products and easy work up etc. were obtained giving clear indication on the potentialities of this technique over conventional heating. Thus, microwave induced organic synthesis becomes a part of green chemistry. Now-a-days it is also termed as e-chemistry because it is easy, economic, effective and eco-friendly.

## MATERIALS AND METHODS

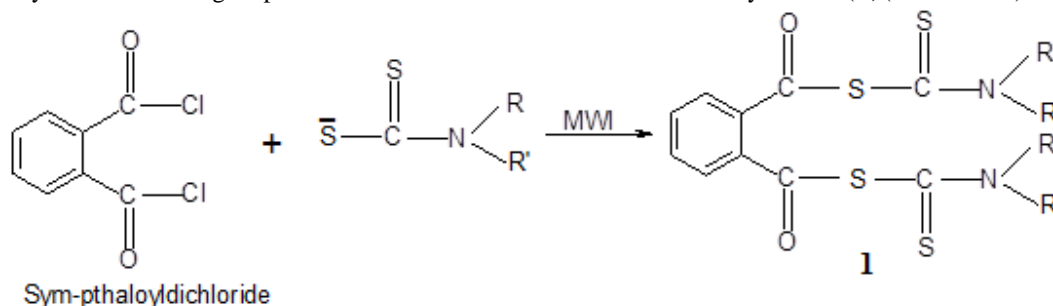
### Materials and Techniques

All starting reagents were purchased from commercial sources and used without further purification. Symmetrical phthaloyl dichloride, unsymmetrical phthaloyl dichloride, dimethylamine dithiocarbamate, diethylamine dithiocarbamate, pyrrolidine dithiocarbamate, piperidine dithiocarbamate, etc. were prepared by reported standard procedures [8-12].

The microwave irradiations were performed using a commercial / kitchen microwave oven model BMO: 700T (BPL- make). All irradiation experiments were carried out using a non-rotating annular photochemical reactor. All melting points were determined on a melting point apparatus and are uncorrected. Infrared (KBr) spectra were recorded on a Perkin-Elmer, Model-137 infrared spectrophotometer and UV spectra were determined on a Beckmann-DB spectrophotometer. NMR spectra were recorded on a Bruker Varian-300 MHz NMR spectrometer in  $\text{CDCl}_3$  with TMS as an internal standard. The chemical shifts are expressed in  $\delta$ -scale downfield from TMS and proton signals are indicated as *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *m* = multiplet. The TLC was run on silica gel plates using acetone-benzene (1:3) as the irrigant. All compounds were analysed satisfactorily for C, H, S and N using Carl-Ebra 1106 elemental analyser in micro analytical laboratory.

### (a) Synthesis of Symmetrical Phthalic bis-amine Dithiocarbamic Anhydride:

A solution of amine dithiocarbamic anhydride in ether was gradually added to an ether solution of symmetrical phthaloyl dichloride at 300K over 5 minutes in microwave oven. The mixture was washed with water to remove any unchanged amine dithiocarbamate and the ether solution was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Removal of the solvent under vacuum gave a product which recrystallized from a mixture (1:1) of ether and methylene chloride to give phthalic bis-amine dithiocarbamic anhydrides (**1**) (Scheme-1).

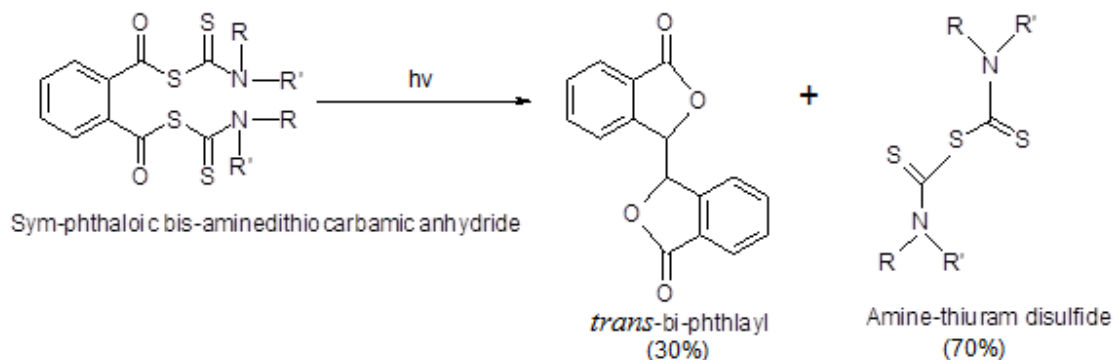


Scheme-1: Synthesis of Symmetrical Phthalic bis-amine Dithiocarbamic Anhydrides

### (b) Photolysis of phthalic Bis-amine dithiocarbamic anhydride

A solution of synthesized phthalic Bis-amine dithiocarbamic anhydride in dry benzene was irradiated for one hour around 278K. Removal of solvent under vacuum gave a residue which on treatment with methylene chloride gave trans-biphthalyl, m.p. 625-627K after recrystallization from acetic acid.

Further, the removal of solvent from the methylene chloride soluble fraction gave amine thiuram disulfide, m.p. 417K, on crystallization from a mixture (1:1) of ether and methylene chloride (Scheme-2).



Scheme-2: Photolysis of phthaloic bis-amine dithiocarbamic anhydrides

## RESULTS AND DISCUSSION

### Analytical and Spectral Characterisation of Phthaloic bis-pyrrolidine dithiocarbamic anhydride (1a):

**Molecular Formula:** C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>S<sub>4</sub>; **Molecular Mass:** 424u

**Analytical Data:**

calculated: %C = 50.94    %H = 04.72    %N = 06.60    %S = 30.18

Found:                    57.85            03.50            06.55            25.80

IR Spectrum (KBr) [ $\nu_{\max}$ ] = 1675cm<sup>-1</sup> (C=O group) and 1471cm<sup>-1</sup> (C=S).

UV Spectrum (CH<sub>2</sub>Cl<sub>2</sub>) [ $\lambda_{\max}$ ] = 290nm, ( $\epsilon$ , 31,100) and 410nm, ( $\epsilon$ , 400).

### Analytical and Spectral Characterisation of Phthaloic bis-piperidine dithiocarbamic anhydride (1b):

**Molecular Formula:** C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>S<sub>4</sub>; **Molecular Mass:** 452u

**Analytical Data:**

calculated:            %C = 53.09            %H = 05.31            %N = 06.19            %S = 28.32

Found:                    53.15                    05.20                    06.20                    28.30

IR Spectrum (KBr) [ $\nu_{\max}$ ] = 1684cm<sup>-1</sup> (C=O group) and 1471cm<sup>-1</sup> (C=S).

UV Spectrum (CH<sub>2</sub>Cl<sub>2</sub>) [ $\lambda_{\max}$ ] = 296nm, ( $\epsilon$ , 18,700) and 410nm, ( $\epsilon$ , 500).

NMR Spectrum (CDCl<sub>3</sub>):  $\delta$  = 4.41ppm (8H), 1.73ppm (12H) and 7.5ppm (4H, aromatic).

### Analytical and Spectral Characterisation of Phthaloic bis-Dimethylamine dithiocarbamic anhydride (1c):

**Molecular Formula:** C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>S<sub>4</sub>; **Molecular Mass:** 372u

**Analytical Data:**

Calculated:            %C = 45.16            %H = 04.30            %N = 07.52            %S = 34.41

Found:                    45.20                    04.40                    07.40                    34.35

IR Spectrum (KBr) [ $\nu_{\max}$ ] = 1686cm<sup>-1</sup> (C=O group) and 1493cm<sup>-1</sup> (C=S).

UV Spectrum (CH<sub>2</sub>Cl<sub>2</sub>) [ $\lambda_{\max}$ ] = 290nm, ( $\epsilon$ , 32,900) and 410nm, ( $\epsilon$ , 600).

### Analytical and Spectral Characterisation of Phthaloic bis-Diethylamine dithiocarbamic anhydride (1d):

**Molecular Formula:** C<sub>18</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>S<sub>4</sub>; **Molecular Mass:** 428u

**Analytical Data:**

Calculated:            %C = 50.46            %H = 05.61            %N = 06.54            %S = 29.91

Found:                    50.25                    05.60                    06.72                    29.85

IR Spectrum (KBr) [ $\nu_{\max}$ ] = 1686cm<sup>-1</sup> (C=O group) and 1476cm<sup>-1</sup> (C=S).

UV Spectrum (C<sub>2</sub>H<sub>5</sub>OH) [ $\lambda_{\max}$ ] = 290nm, ( $\epsilon$ , 24,300) and 410nm, ( $\epsilon$ , 250).

NMR Spectrum (CDCl<sub>3</sub>): δ= triplets at 1.31ppm (12H, methyl), quartet at 3.9ppm (8H, methylene) and multiplet at 7.63ppm (4H, aromatic of an A<sub>2</sub>B<sub>2</sub> pattern).

**Table-1: Comparison of % yield of synthesized compounds**

Compound	m.p (in K)	% Yield	
		Classical method	Green method
1a	413	68	79
1b	406	66	82
1c	389	53	76
1d	360	76	92

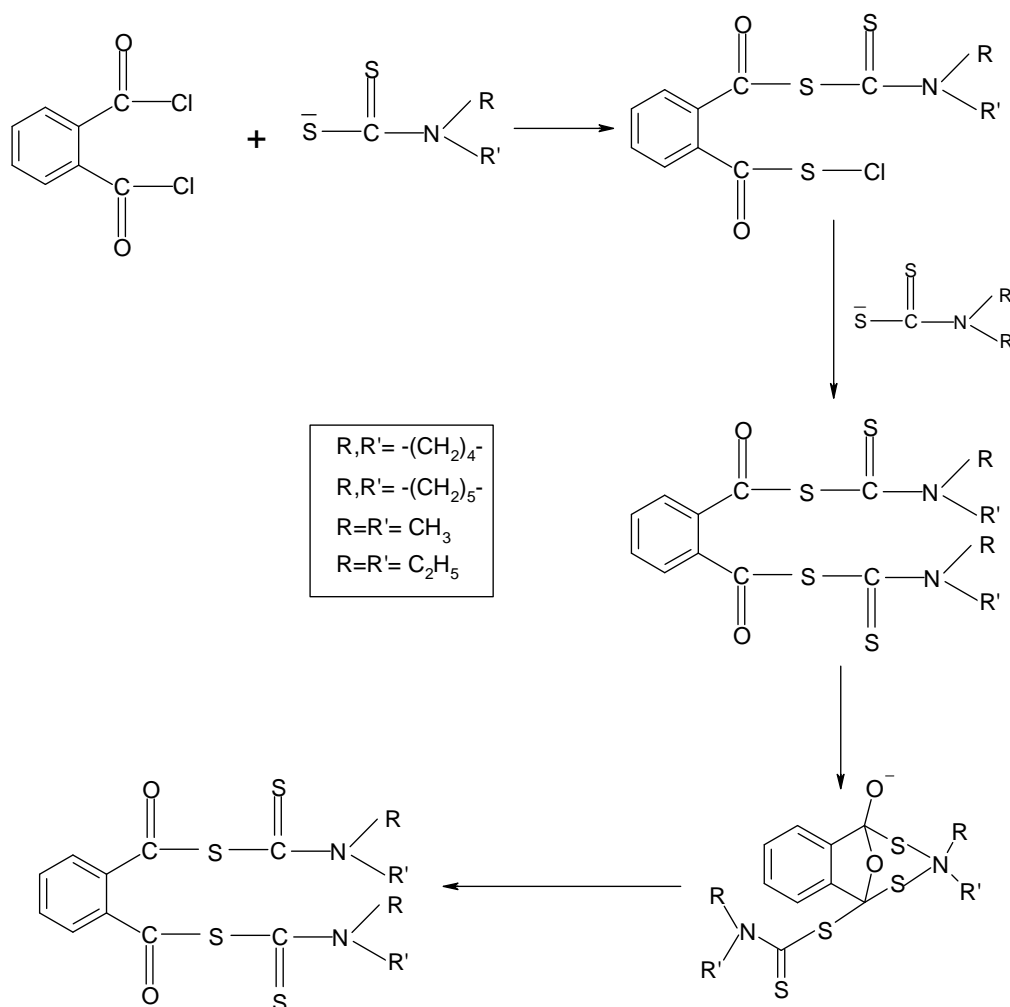
**Table-2: The % yield of photolysed compounds**

Compound	% Yield	
	trans-biphthalyl	thiuram disulfide
1a	30	75
1b	46	40
1c	37	48
1d	33	42

In our present efforts at preparing the symmetrical dixanthates of the type **1**, we have examined the reactions of symmetrical phthaloyl dichloride with a few amine dithiocarbamates. The reaction of symmetrical phthaloyl dichloride with pyrrolidine dithiocarbamate, for example, gave a 92% yield of a product, m.p. 414K and identified as symmetrical phthalic bis-pyrrolidine dithiocarbamic anhydride (**1a**) (**scheme-3**). The identity of **1a** was continued on the basis of analytical results and spectral data. The infrared spectrum of **1a** showed a characteristic absorption band at 1471 cm<sup>-1</sup> due to the C=S group [13]. The ultraviolet absorption spectrum of **1a** was characterized by two absorption maxima at 290 nm (ε, 31,100) and 410 nm (ε, 400). The absorption characteristics of **1a** are quite similar to those of the analogous benzoic piperidine dithiocarbamic anhydrides.

The NMR spectrum (**Figure-1**) of **1a** shows two multiplets at 2.17 ppm (8H) and 3.9 ppm (8H). Of these, the peak at 2.17 ppm is assigned to the methylene protons, away from the nitrogen atom, whereas, the one at 3.9 ppm is due to the methylene protons adjacent to the nitrogen atoms of the pyrrolidine rings. The aromatic protons appear as a multiplet centered around 7.69 ppm (4H), characteristic of an A<sub>2</sub>B<sub>2</sub> system [14].

Our next objective was to study the reaction of the symmetrical phthaloyl dichloride with amine dithiocarbamates with a view to understanding the mode of these reactions. The formation of the symmetrical isomer **1a** in this reaction clearly indicates that the preferred mode of attack of the nucleophile is on the carbonyl carbon of symmetrical phthaloyl dichloride and not on the carbon atom attached to the halogen atoms (**scheme-3**). In continuation of our studies, we have examined the reactions of a few other amine dithiocarbamates with symmetrical phthaloyl dichloride [15]. The reaction of symmetrical phthaloyl dichloride with piperidine dithiocarbamate, dimethylamine dithiocarbamate and diethylamine dithiocarbamate gave the corresponding symmetrical phthalic bis-amine dithiocarbamic anhydrides, **1b**, **1c** and **1d**, in yields ranging between 78—93%.



**Scheme-3: Mechanism of synthesis of symmetrical phthalic bis-amine dithiocarbamic anhydrides**

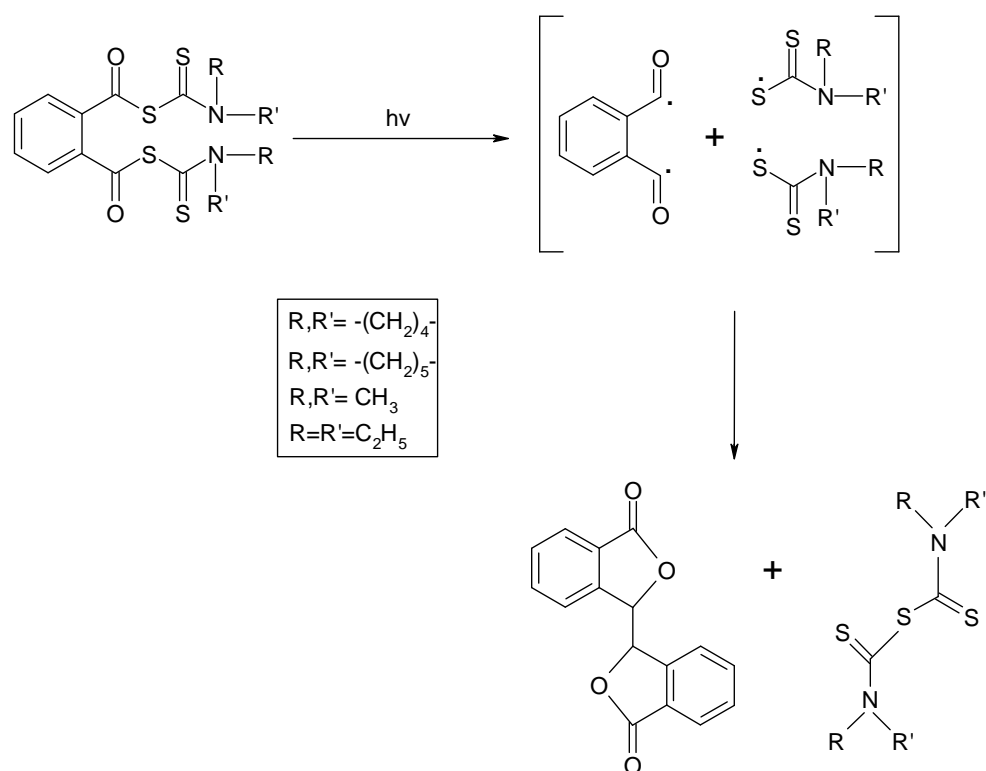
It is interesting to note that the C-S bond fission of the type postulated for the fragmentation of acyl and aroyl xanthates has also been suggested for the photolysis of dithiocarbamic anhydrides. Thus, in the photolysis of benzoic-piperidine dithiocarbamic anhydride, a mixture of products such as benzoic acid, benzoyl piperidine, benzoyl cyclopentamethylene thiocarbamyl disulfide and cyclopentamethylene thiuram bisulfide are formed. A free-radical mechanism has been suggested to account for the formation of these products.

In the present investigation, we have examined the photolysis of a few symmetrical phthalic bis-amine dithiocarbamic anhydrides with a view to studying the nature of the products formed in these reactions.

The photolysis of symmetrical phthalic bis-pyrrolidine dithiocarbamic anhydride (**1a**) for example, gives rise to a mixture of *trans*-biphtalyl in 30% yield and pyrrolidine thiuram disulfide in 73% yield.

The formation of both photolysed products can be explained on the basis of C-S bond fission as in **1a**, giving rise to the radical intermediates.

The diradical species can isomerize to the carbene intermediate, which then undergoes dimerization to give *trans*-biphtalyl. The formation of thiuram disulfide may arise through the dimerization of the radical species. Similarly, the photolysis of other symmetrical phthalic bis-amine dithiocarbamic anhydrides such as **1b**, **1c** and **1d** gave, in each case, *trans*-biphtalyl and the corresponding thiuram sulfides (**scheme-4**).



Scheme-4: Mechanism of photolysis of phthalic bis-amine dithiocarbamic anhydrides

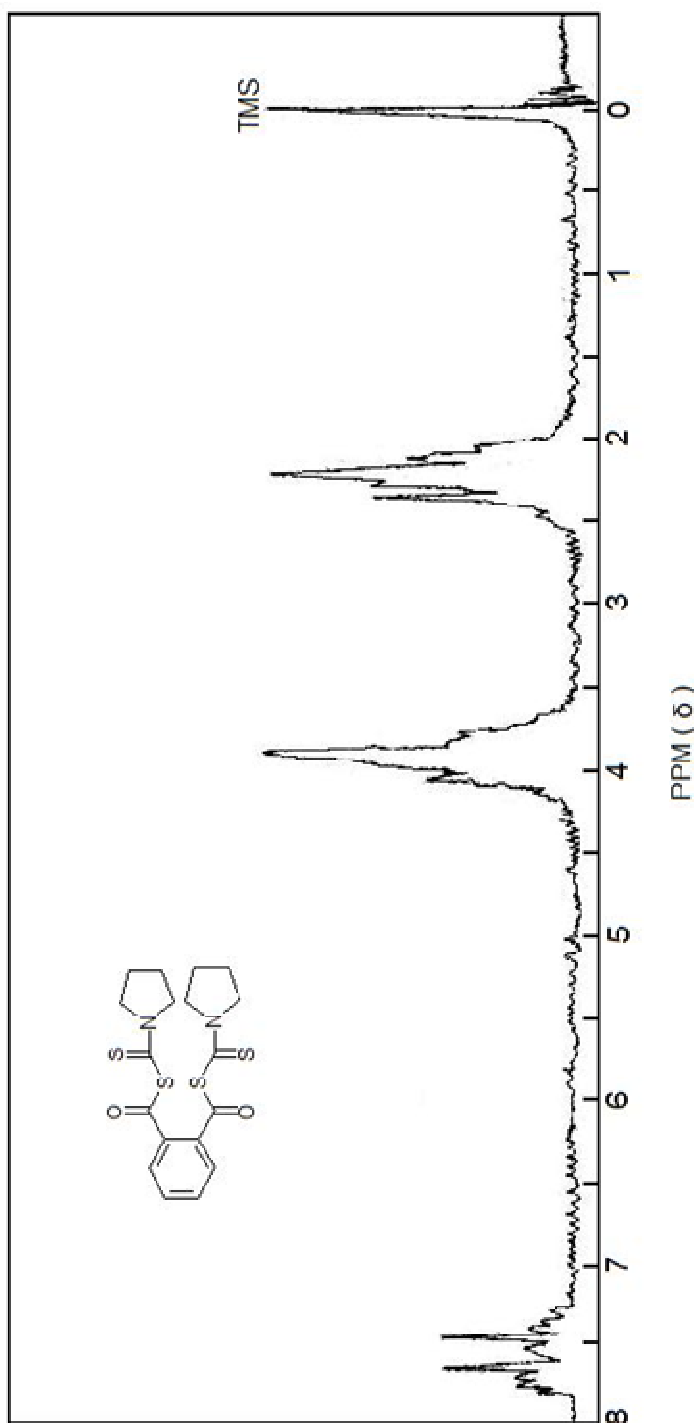


Figure-1: NMR spectrum of symmetrical phthalic bis-pyrrolidine dithiocarbamic anhydride (1a)

#### CONCLUSION

In the present protocol we observed better yields in a shorter period compared to the conventional methods. In conclusion, we have described here an efficient and environmentally benign synthesis of phthalic bis-amine dithiocarbamic anhydrides and their photochemical reactions under microwave irradiation which is simple, mild

and ecofriendly from green chemistry point of view. The photochemical decomposition of phthalic bis-amine dithiocarbamic anhydrides yielded a mixture of several products, consisting of *trans*-biphtalyl and amine thiuram disulfide as major products. The mechanisms of the green synthesis and photochemical reactions have also been presented.

#### Acknowledgement

One of the authors (S.S) would like to acknowledge Late Dr. S.N.Singh for his keen interest and encouragement.

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