

# SYNTHESIS AND APPLICATION OF REACTIVE DYES BASED ON 4, 4'-DIAMINOBENZANILIDE ON VARIOUS FIBRES

<sup>1</sup>Lina A. Patel, <sup>2</sup>Shreyas A. Patel and <sup>3</sup>K. C. Patel  
Assistant Professor, Assistant Professor, Associate Professor,  
Dept. of Chemistry,  
C.U.Shah Science College, Ahmadabad (Gujarat),  
India.

**ABSTRACT:** Ten new monochloro s-triazine reactive dyes have been prepared by coupling tetrazotised 4, 4'-diaminobenzanilide with 3,4-dichloro anilino-cyanurated coupling components and their dyeing performance on silk, wool and cotton fibres has been assessed. All the dyes gave well to very good light fastness on each fiber. Purity of all the dyes was checked by Thin Layer Chromatography (TLC). The structures of all the dyes have been confirmed by Nitrogen Elemental Analysis, FTIR, <sup>1</sup>H-NMR spectra and UV visible spectra. The percentage dye-bath exhaustion on different fibres are reasonable good and acceptable. The dyed fibres displayed moderate to very good fastness to light, washing and rubbing.

**Index Terms -** 4, 4'-diaminobenzanilide, Bisazo reactive dyes, Dyeing, Silk, wool & cotton.

## I. INTRODUCTION

Because of the carcinogenicity of the precursor, it is well accepted that benzidine based dye processing is prohibited. Therefore, systematic study has been carried out to find alternative dyes. The use of benzidine homologs that are less toxic than benzidine can be used in all prior research work [1]. Reactive dyes are colored compounds containing one or two groups capable of forming a covalent bond between the dye ion or molecule's carbon atom or phosphorous atom and the substrate's oxygen atom, nitrogen or sulfur atom of the hydroxyl, amino or mercapto group [2,3]. Patel et al [4-8] have reported fibre reactive dyes for silk, wool and cotton. Due to their greater fixation yield on different fibres, Bisazo reactive dyes have been widely considered. The aim of the present investigation is to obtain reactive dyes with a higher degree of reactivity. The synthesis and analysis of the dyeing properties of bisazo dyes based on 4'-diaminobenzanilide are reported here.

### Material and Method:

All the chemicals were purchased from local market and purified according to established method. Melting points were recorded using VEEGO digital melting point apparatus. The homogeneity and purity of synthesized compounds was established by thin layer chromatography (TLC).

## II. EXPERIMENTAL:

### 2.1. Synthesis of 4, 4'-diaminobenzanilide(A)

#### 2.1.1. Synthesis of *p*-nitro benzoyl chloride:

Mix (10.0 g, 0.06 mole) *p*-nitro benzoic acid with (12.6 g, 0.06 mole) phosphorus pentachloride in a 250 ml RBF. Fit the flask with a calcium chloride guard-tube. Heat the flask on a waterbath, with occasional shaking, until the reaction commences and then for a further 30 minutes or till the vigorous evolution of hydrogen chloride has almost ceased. A pale yellow homogeneous liquid is formed. Remove the phosphorus oxychloride (b.p. 107°C) by heating on an oil bath. Allow to cool and distil the residual liquid under reduced pressure. A small quantity of phosphorus oxychloride passes over first and the temperature rises rapidly to about 150°C; change the receiver and collect the *p*-nitrobenzoyl chloride at 155°C. Pour the product while still fluid into a small-mouthed bottle and allow it to solidify to a yellow crystalline solid, which is obtained by re-crystallization from carbon tetrachloride. Yield 84 %, m.p. 71°C.

#### 2.1.2. Synthesis of 4,4'-dinitrobenzanilide:

Mixture of *p*-nitroaniline (4.0 g, 0.029 mole), 2.4 g of Na<sub>2</sub>CO<sub>3</sub> and 6.3 g of CH<sub>3</sub>COONa in 200 ml of water is treated with 8.5 g of *p*-nitrobenzoyl chloride at 50-60°C for 2 hours with stirring, which on cooling gives 4,4'-dinitrobenzanilide. It was collected, washed and crystallized from glacial acetic acid in yellowish brown needles. Yield 80 %, m.p. 264°C.

#### 2.1.3. Synthesis of 4,4'-diaminobenzanilide

4,4'-dinitrobenzanilide (4.0 g, 0.017 mole) was dissolved in 60 ml of water. The resulting solution was added over a period of 30 minutes to iron turning (4.0 g) with 80 % acetic acid (1 ml) at reflux temperature. When the reduction is completed the reaction mixture was cooled and the liquid residue is then poured in cold water with continuous stirring. The product was filtered and washed thoroughly. 4,4'-diaminobenzanilide was then recrystallized from hot water in a brownish needle form. Yield 80 %, m.p. 204°C.

### 2.2. Tetrazotisation of 4,4'-diaminobenzanilide (B)

4,4'-diaminobenzanilide (2.27 g, 0.01 mole) was suspended in H<sub>2</sub>O (60 ml). Hydrochloric acid (0.86 g) was added drop wise to this well stirred suspension. The mixture was gradually heated up to 70°C, till clear solution was obtained. The solution was cooled to 0-5°C in an ice-bath. A solution of NaNO<sub>2</sub> (0.7 g, 0.01 mole) in water (8 ml) previously cooled to 0°C, was then added over a period of 5 minutes with stirring. The stirring was continued for an hour, maintaining the same temperature, with positive test for nitrous acid on starch iodide paper. After destroying excess of nitrous acid with required amount of a solution of sulphamic acid, the clear tetrazo solution-F at 0-5°C was used for subsequent coupling reaction.

### 2.3. Formation of 3,4-dichloro anilino cyanurated H-acid (C)

#### 2.3.1. Cyanuration of H-acid:

Cyanuric chloride (1.85 g, 0.01 mole) was stirred in acetone (25 ml) at a temperature below 5°C for a period of an hour. A neutral solution of H-acid (3.19 g, 0.01 mole) in aqueous sodium carbonate solution (10% w/v) was then added in small lots over a period of 1 hour. The pH was maintained neutral by simultaneous addition of sodium carbonate solution (1% w/v). The reaction mass was then stirred at 0-5°C for further four hours to obtain a clear solution. The cyanurated H-acid solution thus formed was used for subsequent condensation reaction.

#### 2.3.2. Condensation with 3,4-dichloro aniline (Formation of 3,4-dichloro anilino cyanurated H-acid)

The temperature of ice-cooled well stirred solution of cyanurated H-acid (4.67 g, 0.01 mole) was gradually raised to 45°C for half an hour. To this cyanurated H-acid the 3,4-dichloro aniline (1.62 g, 0.01 mole) was added drop wise at same temperature, over a period of 30 minutes, maintaining the pH neutral by simultaneous addition of sodium bicarbonate (1% w/v). After the addition was completed, stirring was continued for further 3 hours. The 3,4-dichloro anilino cyanurated H-acid solution thus obtained was subsequently used for further coupling reaction.

### 2.4. Coupling of tetrazo (B) solution with 3,4-dichloro-anilino cyanurated H-acid (C) (Formation of dye D<sub>1</sub>)

To an ice cold and stirred solution of 3,4-dichloro anilino cyanurated H-acid (5.92 g, 0.01 mole), a freshly prepared tetrazo solution-F (1.61 g, 0.005 mole) was added dropwise over a period of 10-15 minutes. The pH was maintained at 7.5 to 8.5 by simultaneous addition of sodium carbonate solution (10% w/v). During coupling a purple solution is formed. The stirring was continued for 3-4 hours, maintaining the temperature below 5°C. The reaction mixture was then heated up to 60°C and sodium chloride added until the colouring material was precipitated. It was stirred for an hour, filtered and washed with a small amount of sodium chloride solution (5% w/v). The solid was dried at 80-90°C and extracted with DMF. The dye was precipitated by diluting the DMF-extract with excess of chloroform. A violet dye was then filtered, washed with chloroform and dried at 60°C. Yield 85%. Following the above procedure other reactive dyes D<sub>2</sub> to D<sub>10</sub> were synthesized using various 3,4-dichloroanilino cyanurated coupling components such as J-acid, Gamma acid, Bronner acid, Tobias acid, Koch acid, Sulpho Tobias acid, Laurant acid, N-methyl-J-acid, Chicago acid.

## III. RESULTS AND DISCUSSION:

All the dyes were yellow to brown in colour and obtained in excellent yield (73 to 84 %). The purity of all the dyes has been checked by thin layer chromatography. The absorption spectra of all the dyes were recorded on Beckmann DB-GT Grafting spectrophotometer. The characterization data of dyes are given in (Table-2).

**IR spectra:** IR spectra [10] of all the dyes, in general, showed -N=N stretching vibration at 1600 – 1620 cm<sup>-1</sup>, -C-C- stretching vibration at 1478–1600 cm<sup>-1</sup>, -OH and -NH stretching vibration at 3300–3260 cm<sup>-1</sup>, -C – N stretching vibration at 807–1412 cm<sup>-1</sup>, -S=O stretching vibration at 1039–1190 cm<sup>-1</sup>, -C-Cl stretching vibration at 800 – 820 cm<sup>-1</sup>. Figure-1.

#### **PMR spectra :**

The PMR spectra [11] (300 MHz, DMSO) of D<sub>6</sub> showed signals at 3.35 (4H, -NH), 6.59 – 8.02 (20 H, aromatic proton), 8.75 (1H, -CONH). Figure-2.

#### **DYING OF FIBRES**

All the D<sub>1</sub> to D<sub>10</sub> were applied on silk, wool and cotton fabrics in 2% shade according to the usual procedure [9] in the dye-bath containing the materials listed in (Table – 1).

**Exhaustion and fixation study:** Table report the percentage exhaustion of 2% dyeing on cotton range from 68-76%, for silk range from 67-76% and wool range from 67-78%. The percentage fixation of 2% dyeing on cotton range from 77-91%, for silk range from 77-92% and wool range from 80-90%. (Table - 3)

Dye uptake by the fiber was measured by sampling the dye bath before and after dyeing. The absorbance of the diluted dye solution was measured at λ<sub>max</sub> of the dye. Percentage dye bath exhaustion was calculated using the relationship.

$$\% \text{ Exhaustion} = \frac{\text{Initial O.D.} - \text{Final O.D.}}{\text{Initial O.D.}} \times 100$$

**Fastness properties:** (Table – 4)

**(a) Fastness to washing:** A dyed fabric were stitched between two pieces of undyed fabrics, all of equal length, and then washed at 50 °C for 30 min. The staining on the undyed adjacent fabrics was assessed according to the following gray scale: 1–poor, 2–fair, 3–moderate, and 4–good and 5–excellent.

**(b) Fastness to rubbing:** The dyed fabrics were placed on the base of the Crock meter (Atlas), so that it rested flatly on the abrasive cloth with its long dimension in the direction of rubbing. A square of white testing cloth was allowed to slide on the tested fabrics back and forth twenty times by making ten complete turns of crank. For the wet rubbing test, the testing squares were thoroughly immersed in distilled water. The rest of the procedure was the same as in the dry test. The staining on the white testing cloth was assessed according to the gray scale: 1–poor, 2–fair, 3–moderate, 4–good and 5–excellent.

**(c) Fastness to light:** Light fastness was determined by exposing the dyed fabric for 40 h. The changes in color were assessed according to the following blue scale: 1–poor, 2- slight, 3–moderate, 4- fair, 5–good and 6–very good.

## IV. CONCLUSION

A series of reactive dyes have been synthesized and their colour properties have been examined both in solution and on application to silk, wool and cotton fibres. The dyes give yellow to pink shades on fibres depending upon the coupling component.

## V. ACKNOWLEDGEMENT

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Table – 1: dye-bath materials

Materials	For silk	For wool	For cotton
Fabric (g)	2.0 g	2.0 g	2.0 g
Amount of dye (mg)	40 mg	40 mg	40 mg
Glauber salt (20 %)	1.0 ml	1.5 ml	1.0 ml
Soda ash (10 %)	1.0 ml	----	1.0 ml
pH	3.0	3.0	8.0
MLR	1:40	1:40	1:40
Dyeing time (min)	40 min	60 min	90 min
Dyeing temp. (°C)	85°C	100°C	100°C
Total volume	80 ml	80 ml	80 ml

Table: 2

Dy No	3,4-dichloroanilinoCyanurated couplingComponents (R)	Molecular Formula	Mol. Weight	Yield (%)	%Nitrogen		R <sub>f</sub> Value
					Found	Required	
D <sub>1</sub>	H-acid	C <sub>51</sub> H <sub>27</sub> O <sub>15</sub> N <sub>15</sub> S <sub>4</sub> Cl <sub>6</sub> Na <sub>4</sub>	1523	85	13.72	13.80	0.42
D <sub>2</sub>	J-acid	C <sub>51</sub> H <sub>29</sub> O <sub>9</sub> N <sub>15</sub> S <sub>2</sub> Cl <sub>6</sub> Na <sub>2</sub>	1319	80	15.88	15.93	0.38
D <sub>3</sub>	Gamma acid	C <sub>51</sub> H <sub>29</sub> O <sub>9</sub> N <sub>15</sub> S <sub>2</sub> Cl <sub>6</sub> Na <sub>2</sub>	1319	78	15.85	15.93	0.37
D <sub>4</sub>	Bronner's acid	C <sub>51</sub> H <sub>29</sub> O <sub>7</sub> N <sub>15</sub> S <sub>2</sub> Cl <sub>6</sub> Na <sub>2</sub>	1287	75	16.26	16.33	0.35
D <sub>5</sub>	Tobias acid	C <sub>51</sub> H <sub>31</sub> ON <sub>15</sub> Cl <sub>6</sub>	1083	80	19.35	19.41	0.40
D <sub>6</sub>	Koch acid	C <sub>51</sub> H <sub>25</sub> O <sub>19</sub> N <sub>15</sub> S <sub>6</sub> Cl <sub>6</sub> Na <sub>6</sub>	1695	82	12.32	12.40	0.42
D <sub>7</sub>	Sulpho Tobias acid	C <sub>51</sub> H <sub>29</sub> O <sub>7</sub> N <sub>15</sub> S <sub>2</sub> Cl <sub>6</sub> Na <sub>2</sub>	1287	76	16.25	16.33	0.36
D <sub>8</sub>	Laurant acid	C <sub>51</sub> H <sub>29</sub> O <sub>7</sub> N <sub>15</sub> S <sub>2</sub> Cl <sub>6</sub> Na <sub>2</sub>	1287	78	16.24	16.33	0.42
D <sub>9</sub>	N-methyl-J-acid	C <sub>53</sub> H <sub>33</sub> O <sub>9</sub> N <sub>15</sub> S <sub>2</sub> Cl <sub>6</sub> Na <sub>2</sub>	1347	83	15.55	15.60	0.40
D <sub>10</sub>	Chicago acid	C <sub>51</sub> H <sub>27</sub> O <sub>15</sub> N <sub>15</sub> S <sub>4</sub> Cl <sub>6</sub> Na <sub>4</sub>	1523	80	13.74	13.80	0.38

**Table: 3** :percentage exhaustion and fixation of reactive dyes on silk, wool and cotton

Dye No.	Exhaustion (%)			Fixation (%)		
	S	W	C	S	W	C
D <sub>1</sub>	73.13	71.18	74.50	91.62	80.79	81.88
D <sub>2</sub>	76.45	68.48	71.50	91.56	90.54	81.12
D <sub>3</sub>	75.68	67.78	68.15	85.23	83.36	88.04
D <sub>4</sub>	68.45	75.93	75.05	86.19	80.34	91.94
D <sub>5</sub>	68.50	72.73	73.90	77.37	82.50	85.25
D <sub>6</sub>	71.10	71.70	69.68	90.01	87.87	89.70
D <sub>7</sub>	75.83	72.30	72.05	89.68	90.59	81.19
D <sub>8</sub>	75.93	69.93	70.10	91.54	84.38	87.02
D <sub>9</sub>	74.33	72.85	75.30	82.74	83.05	86.32
D <sub>10</sub>	74.38	75.10	74.50	88.74	82.56	85.91

**Table: 4**

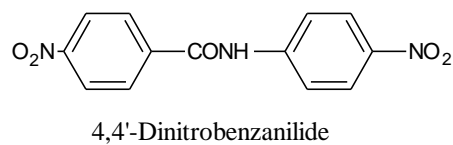
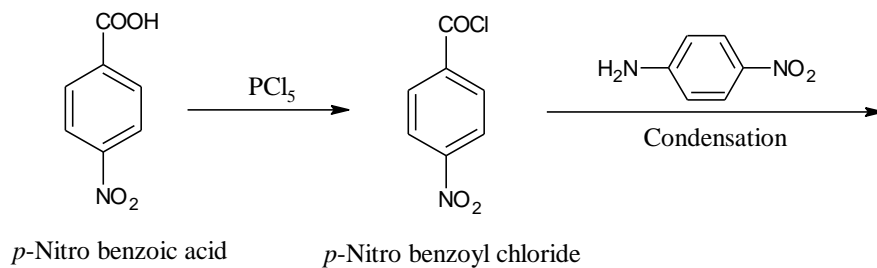
Dye No.	Light fastness			Wash fastness			Rubbing fastness					
	S	W	C	S	W	C	Dry			Wet		
							S	W	C	S	W	C
D <sub>1</sub>	4	5	4	3	4	3	3	4	5	4	3	3
D <sub>2</sub>	6	5	4	4	5	3	3	3	4	4-5	3-4	4
D <sub>3</sub>	4	3	5	5	4	3	6	5	4	5	5	4-5
D <sub>4</sub>	3	5	4-5	4	6	4	5	4-5	2-3	4-5	5	3
D <sub>5</sub>	4	4-5	5	5	4	3	4	3	4	6	4	4
D <sub>6</sub>	4	3	4	3	4	3	4	5	4	5	5-6	4
D <sub>7</sub>	5	4	5	4	3	4	3	4	3-4	4	5	4
D <sub>8</sub>	4	4	4	4-5	4-5	3	6	5	3-4	3	5	4
D <sub>9</sub>	4	5	4	6	4	5	4-5	3-4	3	3	4	4
D <sub>10</sub>	3	4-5	3-4	4	3	5	5	4	5	4	5	4

S= Silk, W= Wool, C= Cotton

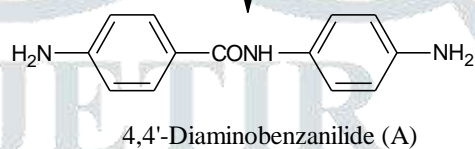


## REACTION SCHEME:

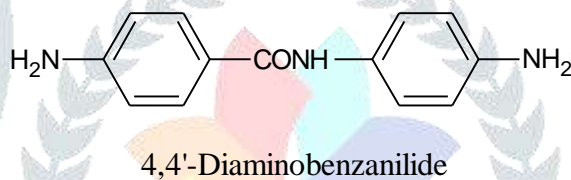
## Synthesis of 4,4'-diaminobenzanilide (A)



Reduction  
Fe + HAc



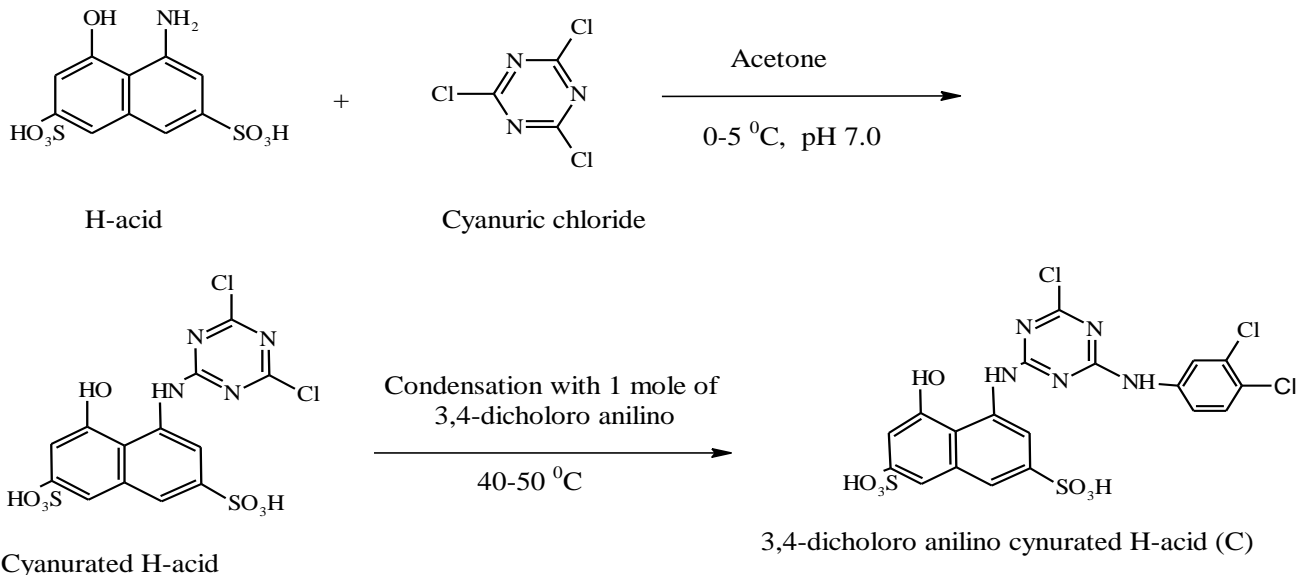
## Tetrazotisation of 4,4'-diaminobenzanilide (B)



Tetrazotisation  
 $\text{NaNO}_2 + \text{HCl}$   
 $0-5^\circ\text{C}$



Synthesis of 3, 4-Dichloro Anilino cyanurated H-acid (C)



Formation of Dyes (D<sub>1</sub> to D<sub>10</sub>):

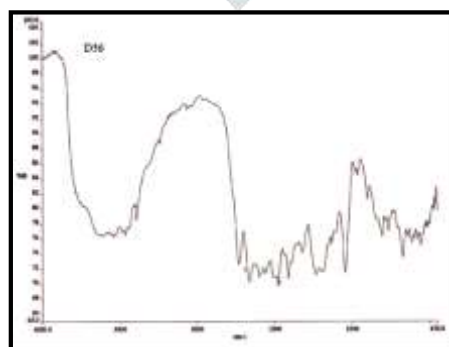
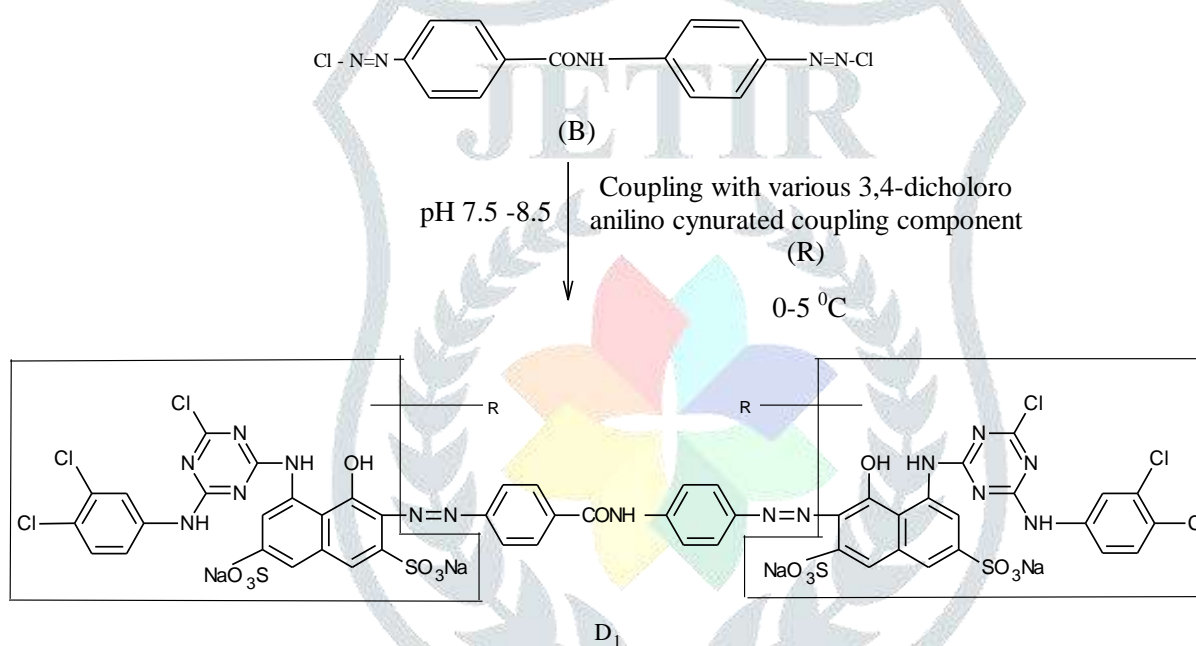
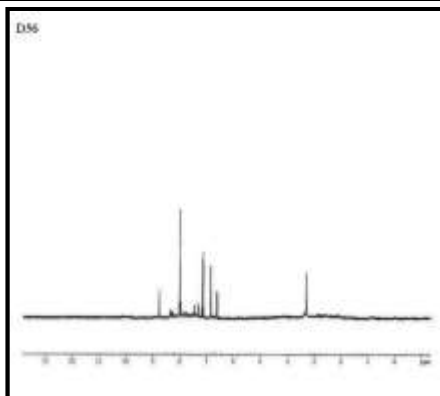


Figure-1: IR spectrum of D<sub>6</sub>



Figure–2: PMR Spectrum of D<sub>6</sub>

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