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SYNTHESIS OF SOME NEW AZO DYES DERIVED FROM 4, 4' -(2, 2, 2-TRICHLOROETHANE -1, 1-DIYL) -BIS (CHLOROBENZENE) AND THEIR BIOLOGICALACTIVITY EVALUATION

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Abstract

In the present study, we report on the synthesis of some new azo dyes 4, 4- (2, 2, 2-trichloroethane-1, 1-diyl) -bis (chlorobenzene) derivatives, their characterization by spectral data (IR, 1H NMR and C13NMR) and evaluation of their biological activity was studied towards two different types of bacteria.

Key words: Azodye, biological activity, environmental treatments.

Introduction

Dyes have a long history and constitute an important component in our daily lives. The dye industry began by using natural plant and insect sources, and then rapidly turned to synthetic manufacturing processes (Bafana *et al.,* 2011), Azo dyes are organic compounds bearing the functional group R-N=N-R', in which R and R2 are usually aryl (Moss *et al.,* 1995). The reason for the stability of the aromatic azo compounds is because they contain the azo group (-N = N-) with a strong double bond.

Azo dyes contain one or more azo groups (-N = N-) which are linked to SP2 hybridized carbon atoms, based on the number of such groups (Zollinger, 2003). The dyes known as monoazo dyes have only one (-N = N-) group while diazo dyes contain two (-N = N-) group, respectively. The azo groups are generally connected to benzene and naphthalene rings, but can also be attached to aromatic heterocycles or enolizable aliphatic groups (Hunger *et al.,* 2000; AL-Ali, 2008). The stability of this type of compound is affected by the type of groups associated on both sides of the azo group and the number of those groups. When the groups contain double elements successively with the double bonds of the azo group and other aromatic groups, they become more stable due to the Resonans (Ghafil, 2008).

Azo dyes are widely used to treat textiles, leather articles and some foods. Chemically related to azo dyes are azo pigments, which are insoluble in water and other solvents (Moss *et al.,* 1995) , Azo dyes are characterized by the presence of a chromophoreazo group. They constitute the largest and most versatile class of synthetic dyes with the greatest variety of colors (Alexander *et al.,* 1999). Azo dyes are considered one of the most important and largest component in the organic preparations for the manufacture of dyes at the present time (Zollinger, 2003). Also, azo dyes are used as a basic material in the following industries: textiles, paper, foodstuffs as a coloring agentused for coloring numerous consumer goods, such as leather, clothes, food, toys, plastics and cosmetics and also has azo compounds that have applications in the manufacture of liquid crystals, Optical connections (Hamon *et al.,* 2009; Gordon, 1990; Kadhim, 2013). Azo compounds are effective Biological in various fields including anti-bacteria (Pathak, 2000) against fungi (Xu *et al.,* 2010) as pesticides (Samadhiya *et al.,* 2001) against viruses (Tonelli *et al.,* 2009) production of resins (Allen *et al.,* 1985) as reagents used at spectrophotometric analysis (Ahlström *et al.,* 2005) medical applications (Thamer, 2011) toner (Patel *et al.,* 2002; Kupradinun *et al.,* 2002), ink-jet printing (Maradiya *et al.,* 2001; Jarad, (2012), This paper covers the preparation of new azo-compounds from 4, 4- (2, 2, 2-trichloroethane-1, 1-diyl) -bis (chlorobenzene) derivativesand their biological activity was investigated.

Experimental :-

1- Synthesis of 1-phenyl-2-(4-(2, 2, 2-trichloro-1-phenylethyl) phenyl) diazenederivatives (1-5):-

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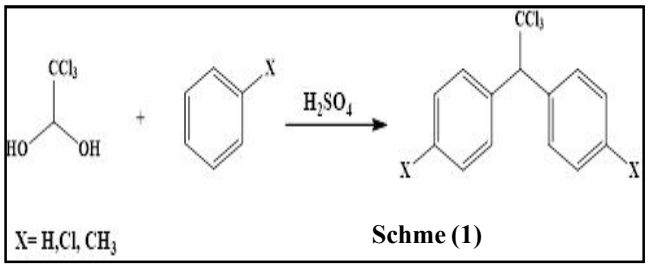


Schme (1)

General procedure:-

In a conical flask, (0.01mol) of aniline derivatives were dissolved in a solution consisting of water and concentrated hydrochloric acid (37%) (1:1) cooled with an ice bath at (0-5)°C for 10 minutes gradually, stirring, adding (0.01mol) From the dissolved sodium nitrite in the least amount of distilled water to the mixture, add the diazonium salt, slowly drop wise, to the compound 2, 2, 2-trichloroethane-1, 1-diyl) bis (chlorobenzene) derivatives dissolved with pyridine. Pigments were obtained in different colors, washed with water and recrystallized from ethanol to give 1, 2, 3, 4, 5.

1-phenyl-2-(3-(2, 2, 2-trichloro-1-phenylethyl) phenyl) diazene (1):-

Dark red powder; yield = 85 %; m.p. = 161-162ºC. *Rf* = 0.44 using petroleum ether : ethyl acetate (1:3) as eluent system.

IR (n/cm^{-1}): 3028, 3008 (C-H), 1643, 1450 (C=C), 1587 (N=N) 1384, 1342 (C-N).

^{1}H NMR (DMSO): d/ppm = 7.74 - 7.72 (d, 2H, o-Ar-H), 7.39 - 7.36 (d, 2H, p- Ar-H), 7.32-7.28 (m, 10H, Ar-H), 5.43 (s, 1H, CH_{alph}).

C_{13} NMR (DMSO): d/ppm = 143.03 (m, 2C, p-Ar), 131.43 - 126.19 (10C, Ar), 102.52 (w, 1C, C-Cl), 62.42 (1C, CH_{alph}).

Anal. Calcd. for $C_{20}H_{15}Cl_3N_2$ (389.70) : C, 61.64; H, 3.88; Cl, 27,29; N, 7.19%. found: C, 61.58; H, 3.80; Cl, 27, 21; N, 7.11%.

1-(4-chlorophenyl)-2-(4-(2, 2, 2-trichloro-1-phenylethyl) phenyl) diazene (2):-

Yellow powder ; yield = 80 %; m.p. = 172-174 ºC. *Rf* = 0.54 using petroleum ether : ethyl acetate (1:4) as eluent system.

IR (n/cm-1): 3013 (C-H), 1656 (C=C), 1582 (N=N) 1243 (C-N), 654 (C-Cl).

^{1}H NMR (DMSO): d/ppm = 8.4-7.28 (m, 13H, Ar-

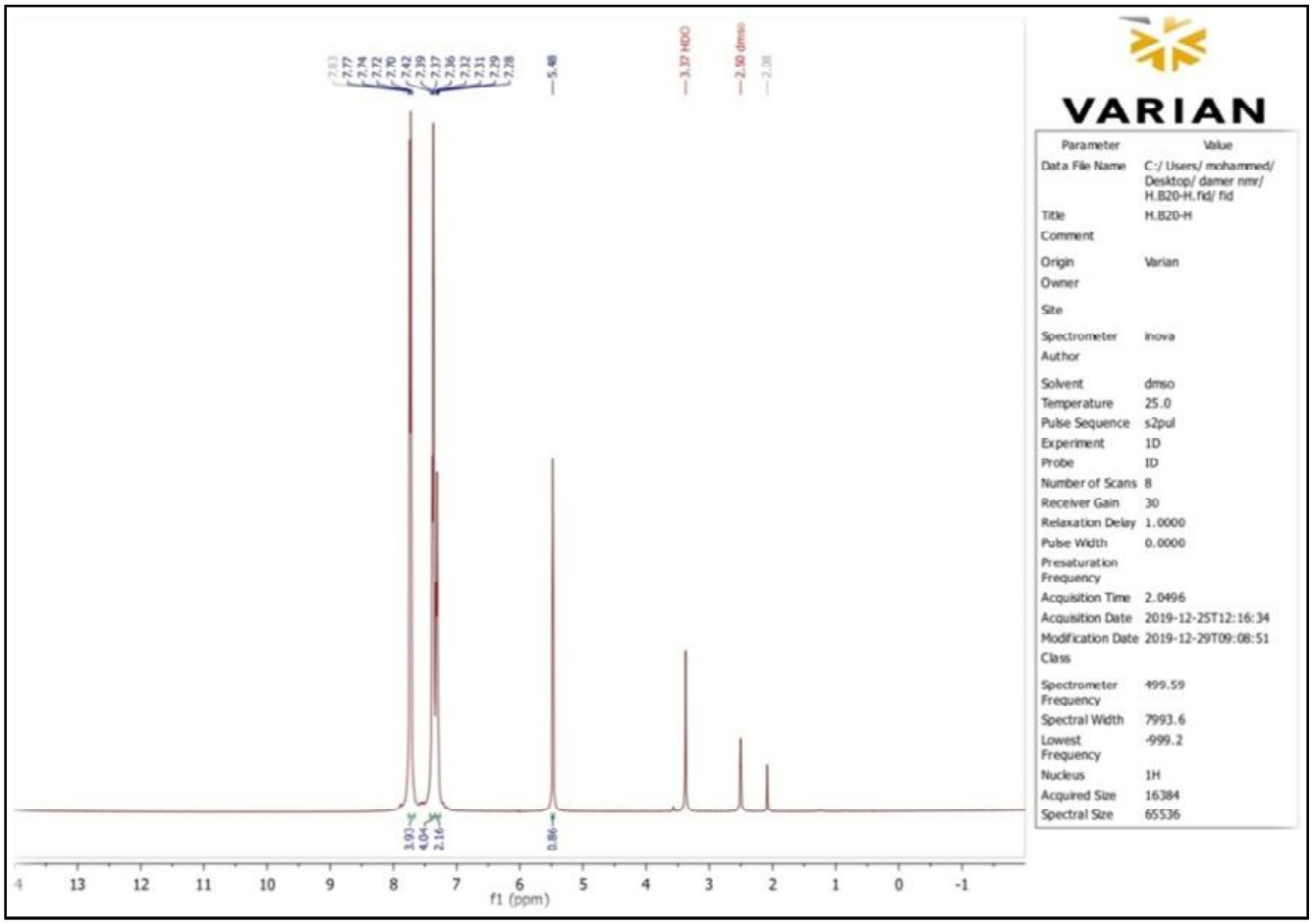
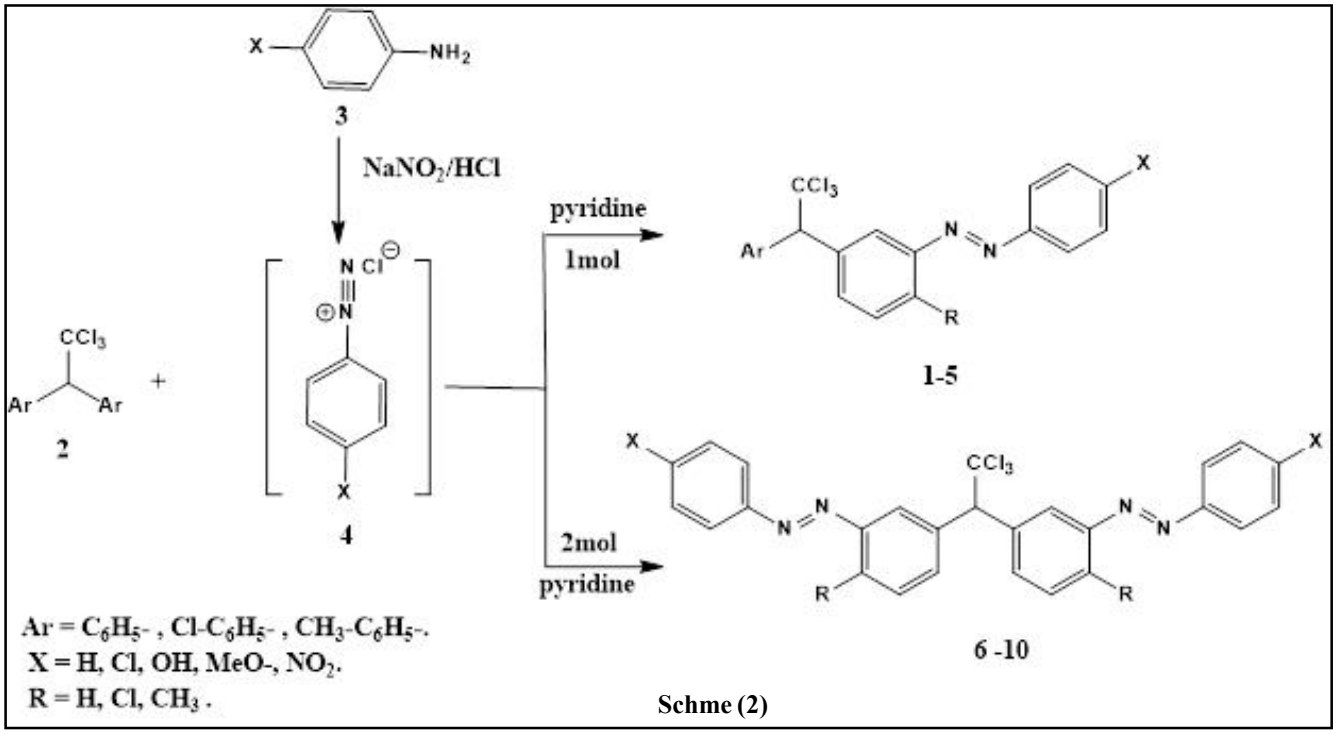


Fig. 1: The H^{1}.NMR Spectrum of compound (1).

H), 6.03 (s, 1H, CH_{alph}).

Anal. Calcd. for $C_{20}H_{14}Cl_4N_2$ (424.15): C, 56.64; H, 3.33; Cl, 33,43; N, 6.61%; found: C, 56.57; H, 3.26; Cl, 33, 34; N, 7.55%.



Schme (2)

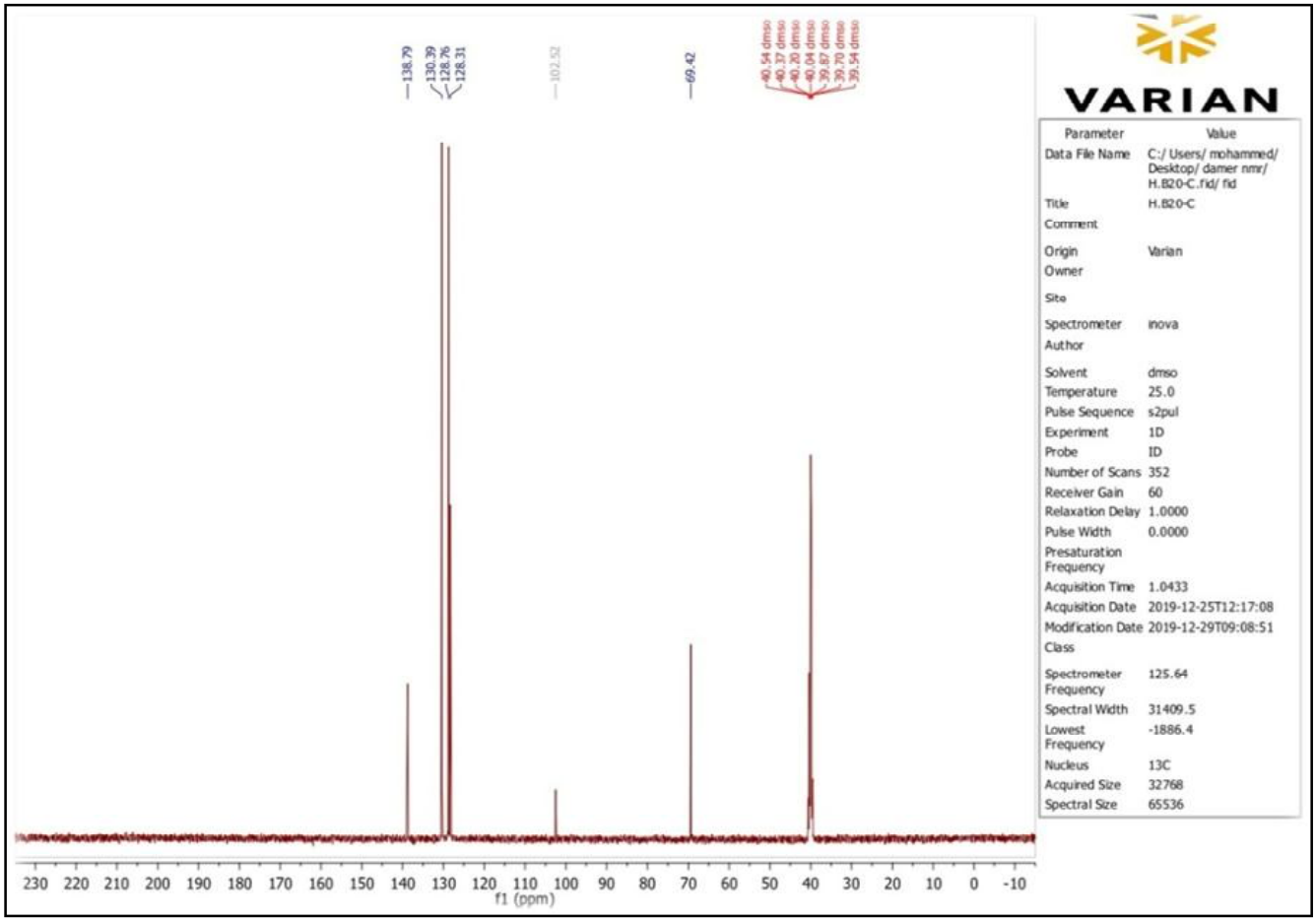


Fig. 2: The C_{13}.NMR Spectrum of compound (1).

4-((2-chloro-5-(2, 2, 2-trichloro-1-(4-chlorophenyl) ethyl) phenyl) diazenyl) phenol (3):-

Brown powder; yield = 72 %; m.p. = 159-160°C. R_f = 0.48 using petroleum ether : ethyl acetate (1:3) as eluent system.

IR ($\bar{\nu}$ /cm^{-1}): 3445 (O-H), 3009 (C-H aromatic), 1665 (C=C), 1590 (N=N), 1322 (C-N), 1216 (C-O), 634 (C-Cl).

^{1}H NMR (DMSO): d/ppm = 9.38 (s, 1H, OH), 7.73-6.96 (m, 11H, Ar-H), 5.54 (s, 1H, CH_{alph}).

Anal. Calcd. for $C_{20}H_{13}Cl_5N_2O$ (474.59): C, 50.62; H, 2.76; Cl, 37,35; N, 5.90; O, 3.37%; found: C, 50.53; H, 2.69; Cl, 37, 29; N, 5.84; O, 3.30%.

1-(4-methoxyphenyl)-2-(2-methyl-5-(2, 2, 2-trichloro-1-(p-tolyl) ethyl) phenyl) diazene (4):-

Yellow powder ; yield = 65 %; m.p. = 152-154ºC. *Rf* = 0.57 using petroleum ether : ethyl acetate (1:3) as eluent system.

IR (n /cm^{-1}): 3012 (C-H, Ar), 2932 (C-H alph), 1651 (C=C), 1587 (N=N), 1237 (C-N), 1210 (C-O), 664 (C-Cl).

^{1}H NMR (DMSO): d/ppm = 7.77 – 7.18 (m, 11H, Ar-H), 6.12 (m, 1H, CH_{alph}), 3.75 (s, 3H, O-CH_3), 2.30, 2.16 (s, 6H, 2C-CH_3).

Anal. Calcd. for C23H21Cl_3N_2O (447.78): C, 61.69; H, 4.73; Cl, 23, 75; N, 6.26, O, 3.57%. found: C, 61.60; H, 4.65; Cl, 23, 66; N, 6.17, O, 3.50%.

4-((2-methyl-5-(2, 2, 2-trichloro-1-(p-tolyl) ethyl) phenyl) diazenyl) phenol (5):

Brown powder ; yield = 67 %; m.p. = 157-158ºC. *Rf* = 0.48 using petroleum ether : ethyl acetate (1:4) as eluent system.

IR (n/cm^{-1}): 3446 (O-H), 3020 (C-H, Ar), 2924 (C-H alph), 1665 (C=C), 1580 (N=N), 1235 (C-N), 1200 (C-O), 668 (C-Cl).

^{1}H NMR (DMSO): d/ppm = 9.24 (w, 1H, OH), 7.73 – 6.78 (m, 11H, Ar-H), 6.18 (m, 1H, CH_{alph}), 2.28, 2.14 (s, 6H, 2C-CH_3).

Anal. Calcd. for C22H19Cl_3N_2O (433.76): C, 60.92; H, 4.42; Cl, 24, 52; N, 6.46; O, 3.69%. found: C, 60.83; H, 4.35; Cl, 24, 43; N, 6.37; O, 3.58%.

2- 4, 4'-((2, 2, 2-trichloroethane-1, 1-diyl) bis

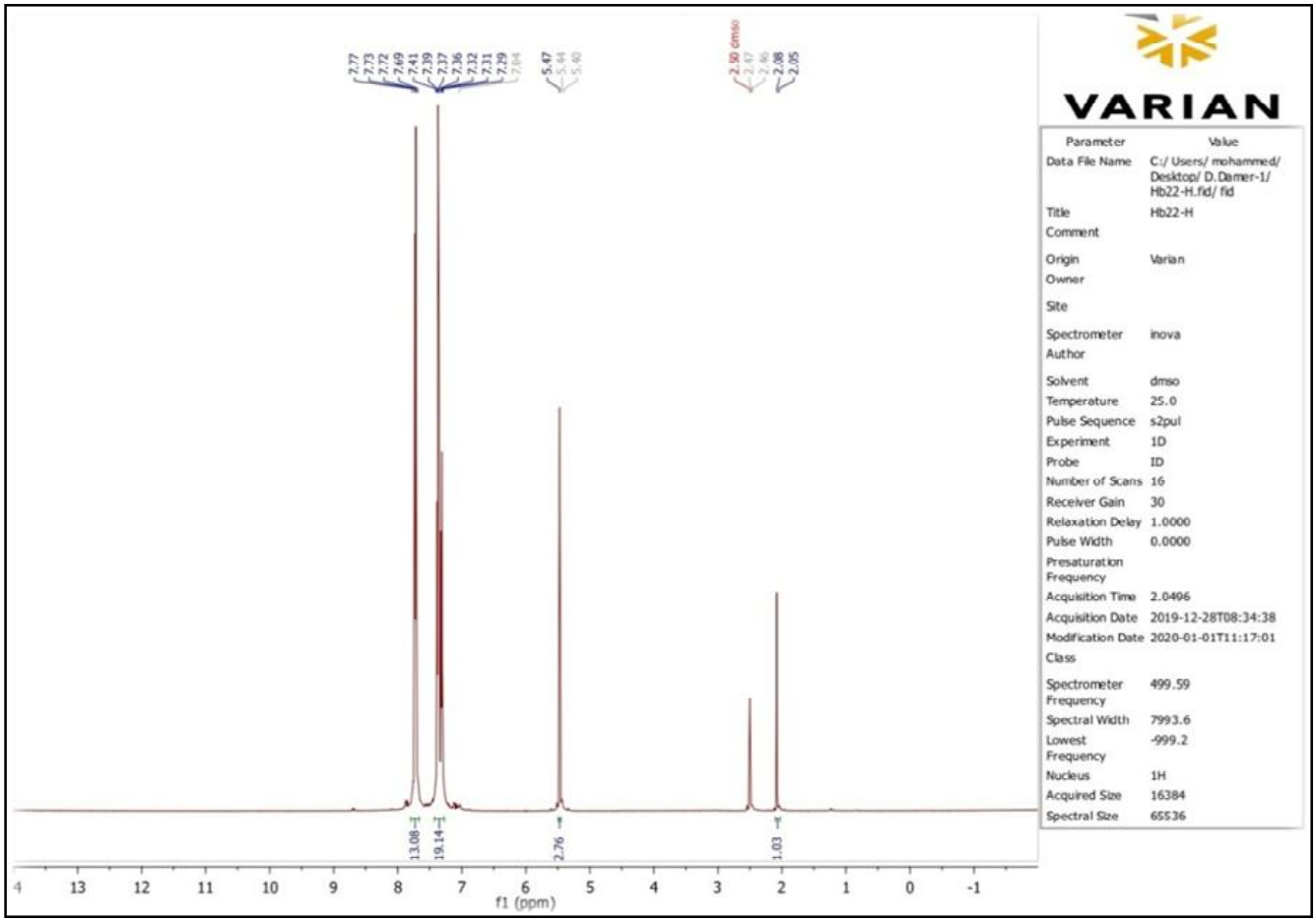


Fig. 3: The H^1.NMR Spectrum of compound (10).

(6-methyl-3, 1-phenylene)) bis (diazene-2, 1-diyl)) diphenol (6):-

General procedure:

A cold solution of sodium nitrite (0.21 g in 10 ml water) was added drop by drop to a cold solution of aniline derivatives (3) (0.47 g, 0.006 mol) in concentrated hydrochloric acid (1.0 ml) with continuous stirring at 0-5ºC. The freshly prepared diazonium salt solution was then added drop wise to a cooled and stirred solution of 4, 4- (2, 2, 2-trichloroethane-1, 1-diyl) -bis (chlorobenzene) (0.85 g, 0.003 mol) and sodium hydroxide solution (0.12g in 10 ml water). The reaction mixture was stirred at 0-5ºC for 2 hours and the resulting precipitate was collected, washed with water and recrystallized from ethanol to give (6-10).

Dark yellow powder; yield = 67%; m.p. = 165-167ºC. *Rf* = 0.68 usingpetroleum ether : ethyl acetate (1:4) as eluent system.

IR (n/cm^{-1}): 3473, 3425 (O-H), 3060, 3043 (C-H), 2945 (C-H, CH_3) 1641, 1448 (C=C), 1581 (N=N), 1340, 1315 (C-N).

^{1}H NMR (DMSO): d/ppm = 9.37(s, 2H, 2OH), 7.78 - 7.42 (d, 4H, o - Ar-H), 7.74 (d, 4H, 2N-C-CH), 6.85-6.26 (m, 4H, CH-C-OH), 5.53 (d, 1H, CH_{alph}).

Anal. Calcd. for $C28H23Cl_3N4O_2$ (553.87) : C, 60.64; H, 4.19; Cl, 19,20; N, 10.12; O, 5.78%. found: C, 60.58; H, 4.10; Cl, 19,14; N, 10.08; O, 5.70%.

2, 2'-((2, 2, 2-trichloroethane-1, 1-diyl) bis (4, 1-phenylene)) bis (1-(4-nitrophenyl) diazene) (7):-

Brownpowder; yield = 73%; m.p. = 179-180ºC. *Rf* = 0.62 using petroleum ether : ethyl acetate (1:4) as eluent system.

IR (n/cm^{-1}): 3061, 3006 (C-H), 1658 (C=C), 1492 (N=N), 1310 (C-N), 576 (C-Cl).

^{1}H NMR (DMSO): d/ppm = 7.77-7.29 (m, 16H, Ar-H), 5.47 (s, 1H, CH_{alph}).

Anal. Calcd. for $C26H17Cl_3N6O_4$ (583.81) : C, 53.49; H, 2.92; Cl, 18, 22; N, 14.40; O, 10.96%. found: C, 53.40; H, 2.83; Cl, 18, 14; N, 14.30; O, 10.87%.

2, 2'-((2, 2, 2-trichloroethane-1, 1-diyl) bis (6-chloro-3, 1-phenylene)) bis (1-(4-nitrophenyl) diazene) (8):-

Brownpowder; yield = 70%; m.p. = 170-171ºC. *Rf* =

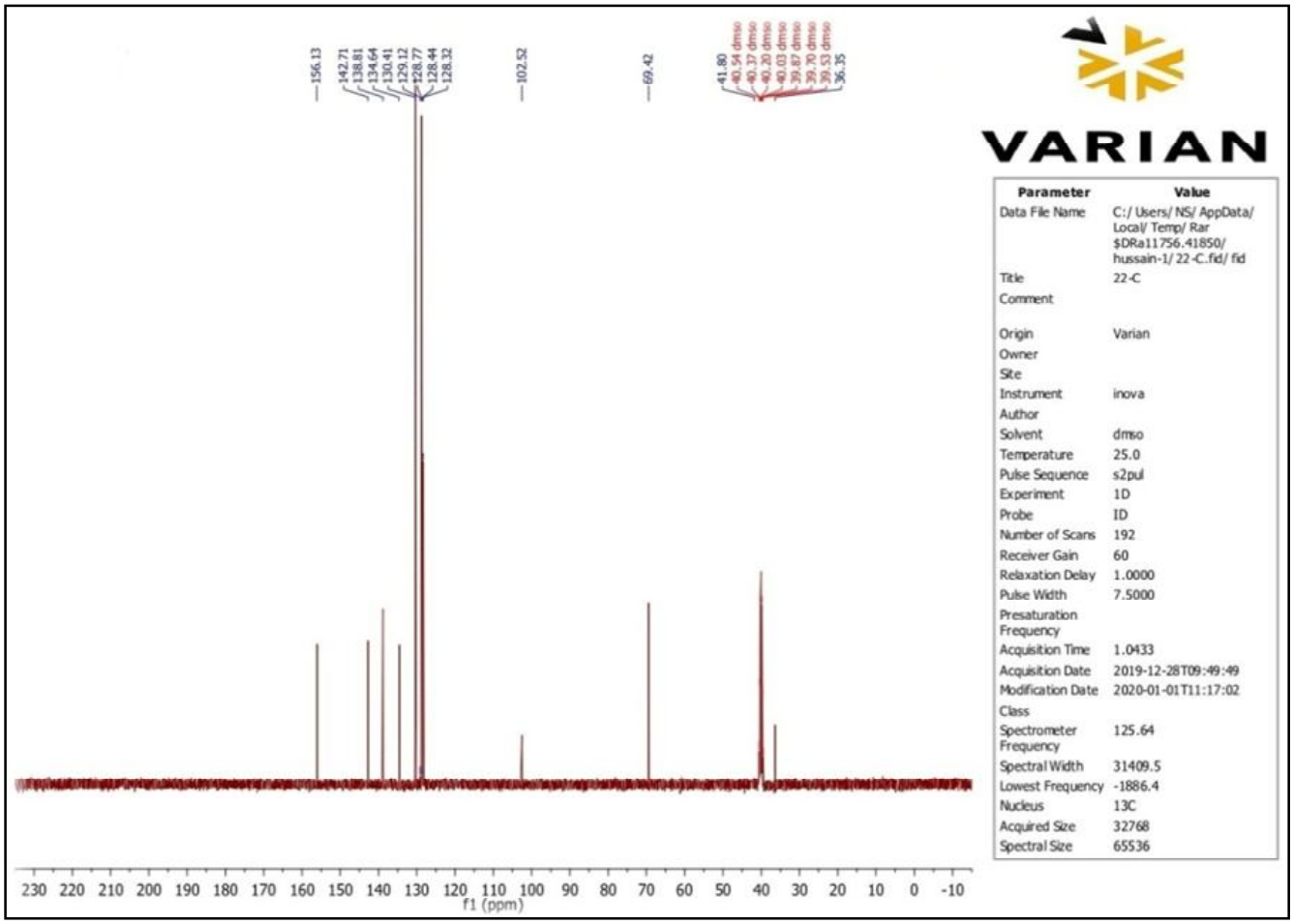


Fig. 4: The C_{13}.NMR Spectrum of compound (10).

Table 3: The antibacterial activity of the prepared compounds in the growth of a number of negative and positive spores (the inhibition circle diameter measured in mm).

Comp. No.	Conc. mg/ml	*Pseudomonas aeruginosa*	*Staphylococcus aureus*
1	1×10^{-4}	+	-
	1×10^{-3}	++	-
	1×10^{-2}	+++	+
2	1×10^{-4}	-	+
	1×10^{-3}	+	++
	1×10^{-2}	++	+++
3	1×10^{-4}	-	+
	1×10^{-3}	+	+++
	1×10^{-2}	++	+++
4	1×10^{-4}	-	-
	1×10^{-3}	-	-
	1×10^{-2}	+	++
5	1×10^{-4}	++	-
	1×10^{-3}	++	+
	1×10^{-2}	+++	++
6	1×10^{-4}	+	-
	1×10^{-3}	+	+
	1×10^{-2}	++	++
7	1×10^{-4}	+	-
	1×10^{-3}	++	+
	1×10^{-2}	+++	++
8	1×10^{-4}	+	+
	1×10^{-3}	++	++
	1×10^{-2}	++	+++
9	1×10^{-4}	-	+
	1×10^{-3}	+	+++
	1×10^{-2}	++	+++
10	1×10^{-4}	+	+
	1×10^{-3}	++	++
	1×10^{-2}	++	+++

No inhibition **(-)** = Inhibition (5-10) mm **(+)** = Inhibition (15-20) mm **(++)** = Inhibition (25-30) mm **(+++)** =

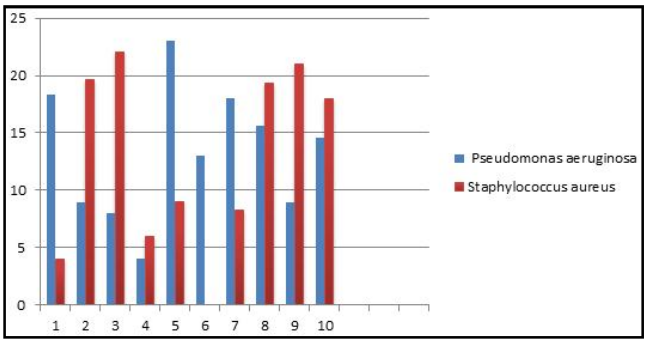
0.60 using petroleum ether : ethyl acetate (1:4) as eluent system.

IR (n/cm^{-1}): 3051, 3011 (C-H), 1662 (C=C), 1490 (N=N), 1340 (N-O), 1200 (C-N), 679 (C-Cl).

^{1}H NMR (DMSO): d/ppm = 8.38-7.30 (m, 14H, Ar-H), 6.14 (s, 1H, CH_{alph}).

C_{13} NMR (DMSO): d/ppm = 154.50 (m, 2C, C-N=N), 149.43 (m, 2C, C-NO_2), 139.83 (m, 2C, CH-Ar), 136.56 – 119.56 (m, 14C, Ar) 102.05 (w, 1C, C-Cl), 65.53 (1C, CH_{alph}).

Anal. Calcd. for $C_{26}H_{15}Cl_5N_6O_4$ (652.69) : C, 47.85; H, 2.32; Cl, 27, 16; N, 12.88; O, 9.80%. found: C, 47.71; H, 2.25; Cl, 27, 05; N, 12.80; O, 9.71%.



2, 2'-((2, 2, 2-trichloroethane-1, 1-diyl) bis (6-chloro-3, 1-phenylene)) bis (1-(4-methoxyphenyl) diazene) (9):-

Brown powder; yield = 68%; m.p. = 163-164ºC. *Rf* = 0.61 using petroleum ether : ethyl acetate (1:4) as eluent system.

IR (n/cm^{-1}): 3024 (C-H) Ar, 2923 (C-H) CH3, 1645 (C=C), 1449 (N=N), 1246 (C-OMe), 1200 (C-N), 677 (C-Cl).

^{1}H NMR (DMSO): d/ppm = 7.78-7.29 (m, 14H, Ar), 6.17 (s, 1H, CH_{alph}), 3.39 (m, 6H, $2CH_3$).

Anal. Calcd. for $C_{28}H_{23}Cl_5N_4O_2$ (622.75) : C, 54.00; H, 3.40; Cl, 28, 46; N, 9.00; O, 5.14%. found: C, 49.91; H, 3.33; Cl, 28, 33; N, 8.93; O, 5.02%.

2, 2'-((2, 2, 2-trichloroethane-1, 1-diyl) bis (3, 1-phenylene)) bis (1-(p-tolyl) diazene) (10):-

Yellowpowder; yield = 74%; m.p. = 155-156ºC. *Rf* = 0.62 using petroleum ether : ethyl acetate (1:4) as eluent system.

IR (n/cm^{-1}): 3051, 3011 (C-H), 1662 (C=C), 1490 (N=N), 1340 (N-O), 1200 (C-N), 679 (C-Cl).

^{1}H NMR (DMSO): d/ppm = 7.77 - 7.29 (m, 16H, Ar-H), 5.44 (m, 1H, CH_{alph}), 2.08, 2.05 (m, 6H, $2CH_3$).

C_{13} NMR (DMSO): d/ppm = 156.13 (m, 4C, C-N=N), 142.71 (m, 2C, C- CH_3), 138.81 (m, 2C, CH-Ar), 134.56 – 128.32 (m, 16C, Ar) 102.05 (w, 1C, C-Cl), 69.42 (1C, CH_{alph}), 36.34 (m, 2C, $2CH_3$).

Anal. Calcd. for $C_{26}H_{15}Cl_5N_6O_4$ (521.87) : C, 64.44; H, 4.44; Cl, 20, 38; N, 10.74. found: C, 64.37; H, 4.38; Cl, 20, 29; N, 10.68.

Results and Discussion

The key compound dichlorodiphenyltrichloroethane (2) was prepared using a known method exploiting the reaction of chlorobenzene with chlorohydrit (1) and sulfuric acid (Scheme 1).

In order to explore the potential of compound 2 in synthesis, the diazocoupling reaction of dichlorodiphenyltrichloroethane (2) with benzenediazonim chloride (4) (in situ prepared from diazotization of aniline (3) with

$NaNO_2$ in the presence of concentrated HCl) was also investigated. The reaction can be accomplished at temperature 0-5°C to afford 1- (2-chloro-5-(2, 2, 2-trichloro-1-(4-chlorophenyl) ethyl) phenyl)-2-phenyldiazene (1-5), (6-10) in good yield as shown in Scheme (2).

Evaluation of the biological activity of some of the prepared compounds:

The organic chlorine compounds and the derived azo compounds are characterized by a differentiated biological activity in the direction of the positive bacteria for the dye of cram and negative for the dye, It is as follows:

1- Pseudomonas aeruginosa.

2- Staphylococcus aureus.

These germs were chosen due to their medical importance as they cause many diseases, in addition to that they differ in their resistance to antibiotics. The biological effectiveness of some of the prepared compounds was evaluated using the method of drilling (1) and measuring the level of inhibition zone (the results indicate that the prepared compounds It has the ability to inhibit the growth of bacteria used in both positive and negative types of dye Cram in different proportions, as in table 3.

Where we note from the chart below the rates of inhibition in relation to the compounds whose biological activity was evaluated, where compound (5) showed the highest rate of inhibition of the direction of Pseudomonas aeruginosa followed by compound (1, 7, 8, 10 and 6) and the lowest inhibition ratio showed by compound (4), either The damping ratios of the compounds above the direction of Staphylococcus aureus, so the highest inhibition ratio was for compound (3, 9, 810 and 2), the lowest for compound (6, 1).

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