Synthesis and spectroscopic studies of charge- transfer complexes of 1H-1,2,4-triazole with some π acceptors in different solvents.

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Abstract

The reactions between 1H-1,2,4-triazole (TR) with chloranilic acid (CAA), 3,5-dinitrobenzoic acid (DNBA), 4-hydroxybenzoic acid (PHB) and 1,3-dinitrobenzene (MDNB) have been studied in MeOH at room temperature by FT- IR, ^{1}H NMR spectrometer, Fluorescence Spectra, conductivity measurements and XRD of the reactions. The data obtained indicate the formation of 1:1 charge-transfer complexes [(TR) (MDNB)], [(TR) (DNBA)], [(TR) (PHB)] and [(TR) (CAA)], and also indicate a charge- transfer interaction associated with a proton migration from the acceptor to the donor followed by intermolecular hydrogen bonding. The FT- IR spectra of the complexes showed a considerable shift in absorption peaks, changes in intensities of the peaks and formation of a new band (probably due to hydrogen bonding) on complexation.

Keywords: 1H-1,2,4-triazole; Fluorescence; X- Ray Diffraction; Nuclear Magnetic Resonance (NMR);

1. Introduction: –

Charge-transfer complexation phenomenon, introduced by Mulliken [1], was discussed widely by Foster. Electron donor–acceptor (EDA) or charge-transfer complexes (CTCs) are recently gaining importance as potential high efficiency non-linear optical materials [2], organic superconductors [3-4] as well as photo catalysts [5]. Charge transfer complexes play an important role in many biological systems, for examples the transfer of charge from one molecule to another during drug action, enzyme catalysis and drug– receptor binding mechanism [6-7], in solar energy storage and in surface chemistry [8] as well as in many biological fields [9-11]. On the other hand, the charge transfer reactions of certain π -acceptors have been successfully utilized in pharmaceutical analysis [12-22]. For these wide applications extensive studies on CT complexes of π-acceptors have been performed [23-28]. CT- interactions between aromatic electron acceptors and electron donors containing nitrogen, oxygen, or sulfur atoms have been reported over the last years [29-31]. CT complexes are being regarded as important materials for use as organic superconductors [32]. The proton-transfer from organic acid to amines may takes place readily with very low activation energy in contrast with the attack of the amine to the carbonyl carbon leading to amide formation [33-34]. Hydrogen bonding and proton transfer processes are abundant in organic chemistry and biochemistry [35-37]. They play an important role in various chemical and biological systems such as

constructing and stabilizing biomolecular and supramolecular structures [38-41]. Although CT complexes of five membered ring compounds with one hetero atom were extensively investigated [42-47], a little information is available in the literature concerning CT complexes of five membered compounds with two or more hetero atoms. 1H-1,2,4-triazole is one of a pair of isometric chemical compounds with molecular formula $C_2H_3N_3$, called triazoles, which have a five- membered ring of two carbon atoms and three nitrogen atoms. 1H-1,2,4-triazole is a basic aromatic heterocycle. 1H-1,2,4-triazole derivatives find use in a wide variety of applications, most notably as antifungals such as fluconazole and itraconazole. 1H-1,2,4-triazole and its derivatives constitute an important class of organic compounds with diverse agricultural, industrial and biological activities [48-49], including anti-microbial [50-51], sedative, anti-convulsant [52] and anti- inflammatory [53]. The present work includes the characterization of charge transfer complexes of 1H-1,2,4-triazole as donor with some acceptors by FT- IR spectrometer, ^{1}H NMR spectra, Fluorescence Spectra and Conductivity.

2. Materials and methods: –

2.1. Materials: –

All chemicals used were of high grade. 1H-1,2,4–triazole (TR) was obtained from (SD Fine Chem. Limited), 4-hydroxybenzoic acid (BDH England); 1,3-dinitrobenzene (MERCK), 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (OHO Chemi), 3,5-dinitrobenzoic acid (OHO Chemi), methanol, acetone, ethanol, DMSO and hexane were obtained from Merck analytical grade and were used without further purification.

2.2. Synthesis of CT complexes: –

2.2.1. Synthesis of CT complex of 1H-1,2,4-triazole (TR) with 4-hydroxybenzoic acid (PHB):

The solid CT complex was prepared by mixing the saturated solution of 1H-1,2,4-triazole (TR) (0.20721 gm, 3mmol) in 20 ml methanol with saturated solution of 4-hydroxybenzoic acid (PHB) (0.51436gm, 3mmol) in 20 ml methanol. A pink colored ppt. was formed by stirring for around 10 hours. The precipitate was filtered off and washed several times with small amounts (5ml) of hexane and dried under vacuum over $CaCl_2$. The melting point of the CT complex was measured as 234-236 °C. The white pink crystal was soluble in methanol, double distilled water, acetone and DMSO, but insoluble in hexane and chloroform.

2.2.2. Synthesis of CT complex of 1H-1,2,4-triazole (TR) with 1,3-dinitrobenzene (MDNB):

The solid CT complex was prepared by mixing the saturated solution of 1H-1,2,4-triazole (TR) (0.20721gm, 3mmol) in 20 ml methanol with saturated solution of 1,3-dinitrobenzene (MDNB) (0.16812gm, 3mmol) in 20 ml methanol. A lemon chiffon colored ppt. was formed by stirring for around 9 hours. The precipitate was filtered off and washed several times with small amounts (5ml) of hexane

and dried under vacuum over $CaCl_2$. The melting point of the CT complex was measured as 85-86 °C. The lemon chiffon crystal was soluble in methanol, acetone and DMSO, but insoluble in hexane, and chloroform, and partially soluble in double distilled water.

2.2.3. Synthesis of CT complex of 1H-1,2,4-triazole (TR) with 3,5-dinitrobenzoic acid (DNBA):

The solid CT complex was prepared by mixing the saturated solution of 1H-1,2,4-triazole (TR) (0.20721 gm, 3mmol) in 20 ml methanol with saturated solution of 3,5-dinitrobenzoic acid (0.6366gm, 3mmol) in 20 ml methanol. A yellow colored ppt. was formed by stirring for around 9 hours. The precipitate was filtered off and washed several times with small amounts (5 ml) of hexane and dried under vacuum over $CaCl_2$. The melting point of the CT complex was measured as 212-214 °C. The white yellow crystal was soluble in methanol, acetone and DMSO but insoluble in hexane and chloroform, and partially soluble in double distilled water.

2.2.4. Synthesis of CT complex of 1H-1,2,4-triazole (TR) with 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (CAA): –

The solid CT complex was prepared by mixing the saturated solution of 1H-1,2,4-triazole (TR) (0.20721 gm, 3mmol) in 20 ml methanol with saturated solution of 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (CAA) (0.62698gm, 3mmol) in 20 ml methanol. A red colored ppt. was formed by stirring for around 9 hours. The precipitate was filtered off and washed several times with small amounts (5 ml) of hexane and dried under vacuum over $CaCl_2$. The melting point of CT complex was measured as 260-262 °C. The red crystal was soluble in methanol, double distilled water and DMSO but insoluble in hexane, and partially soluble in chloroform and acetone.

3. Results and Discussion: –

Reactions of 1H-1,2,4-triazole (TR) with 4-hydroxybenzoic acid (PHB), 1,3-dinitrobenzene (MDNB), 3,5-dinitrobenzoic acid (DNBA) and 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (CAA) resulted in the formation of stable charge- transfer complexes [(TR) (PHB)], [(TR) (MDNB)], [(TR) (DNBA)], and [(TR) (CAA)] with a donor–acceptor molar ratio of 1:1. The infrared spectra of the reactants and complexes were recorded using KBr discs on Interspec 2020 FT- IR Spectrometer U.K. X-ray diffraction (Rigaku, Japan, Miniflex-II) using Cu-K_α radiation (λ = 1.5418 Å) in 2θ range from 20º to 80º. The proton NMR spectra of the reactants and the formed CT complexes were measured in DMSO using Bruker Advance 11 400 NMR spectrometer. The fluorescence spectra were recorded using instrument model F-2500 FL Spectrophotometer ROM Version 4000.01

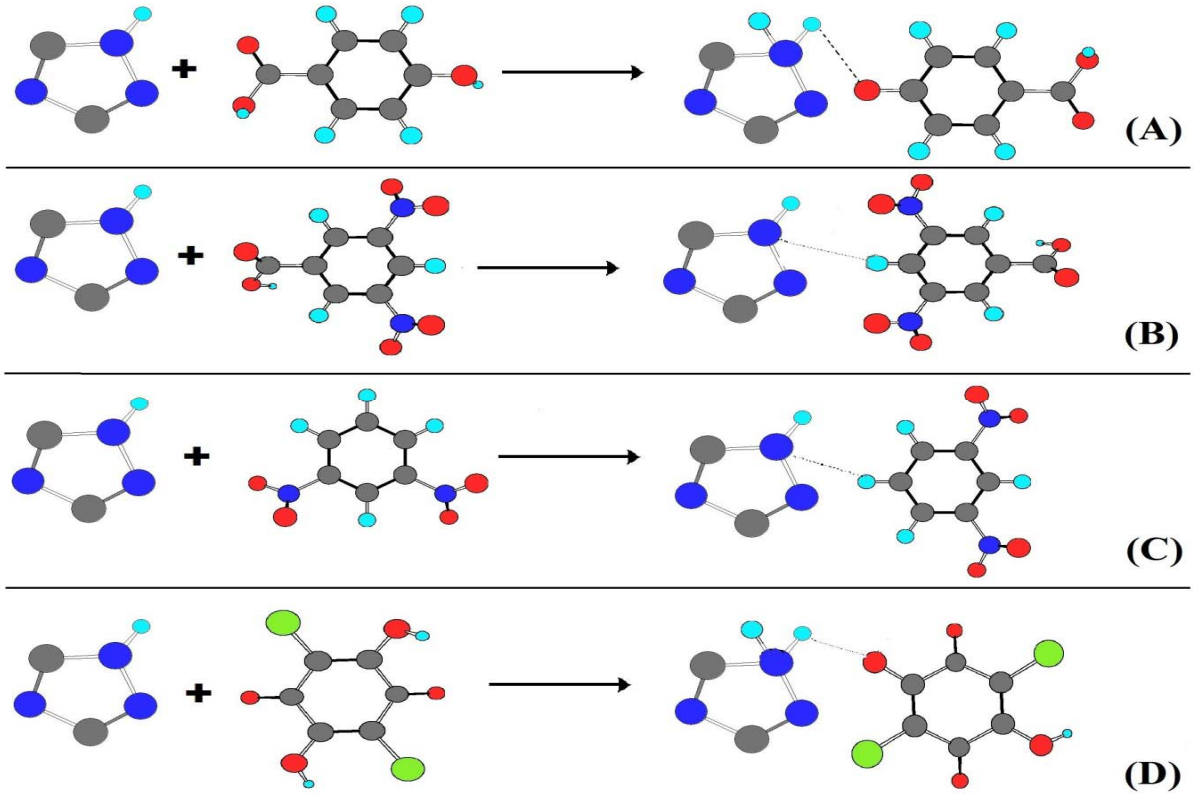
3.1. FT- IR Spectra Studies: –

The infrared spectra of the characterized bands of 1H-1,2,4-triazole– 4-hydroxybenzoic acid (TR- PHB), 1H-1,2,4-triazole– 1,3-dinitrobenzene (TR– MDNB), 1H-1,2,4-triazole– 3,5-dinitrobenzoic acid (TR– DNBA) and 1H-1,2,4-triazole– 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (TR- CAA) are shown in Figures 1 to 4. The observation of the main infrared bands of the donor: TR and acceptors: MDNB, PHB, DNBA and CAA in the respective complex spectra strongly support the formation of CT- complexes by intermolecular hydrogen bonding. However, the analytical and spectroscopic data enable us to predict possible structure as shown in Scheme 1. Generally, the results of chemical analysis of the synthesized solid CT complexes (Table 1) indicate the formation of 1:1 CT complexes.

Table 1 Infrared frequencies (cm^{-1}) and tentative assignments for TR, PHB, CAA, DNBA, MDNB and their HBCT complexes.

TR	PHB	CAA	DNBA	MDNB	CT of TR-PHB	CT of TR-CAA	CT of TR-DNBA	CT of TR-MDNB	Assignments
3450	3380	3236			3392	3234	3280	3106	v (O- H), v (N- H)
						3154			
3126	3197			3106	3134	3119			
3034	3062		3096	3050		3047	3095	3050	
2971	2955		2891		2988		2964		H-Bonding
2931	2832		2820	2871	2829	2869	2821	2871	v (C-H); aromatic
2867	2720						2670	2740	
2693	2661		2673	2675	2662	2551	2539		
2559	2546	2600	2538	2486	2547	2363	2350	2610	-C= C- H
				1998					
				1946	1928	1952		1998	
				1898				1946	
1831	1926			1827				1823	
	1787	1655	1704	1767	1789	1746	1706	1767	
1771	1680	1628	1632	1612	1682	1635	1635	1614	-C=N
	1596	1536	1596		1599	1575	1599	I590	v (NO_2)
1640	1509	1508	1541	1529	1508	1531	1543	1529	v (C=C)
1545	1449				1448			1501	
	1418		1414		1420	1436	1416	1488	(C- H) momodef.
	1366	1371	1350	1350	1369	1396	1349	1410	-(C-C), -sNO_2
1330	1318	1320	1300	1310	1317	1361	1304	1342	-(C-N)
1298	1283	1271	1287	1271	1289	1262			
1263	1235	1210		1144	1242	1202	1285	1271	(C-H) in plane bending

	1163			1092	1162	1166		1148	
1179	1128	1174	1179	1068	1103	1043	1182	1092	v(C-NO_2)
1144	1100			1001	1012	988		1064	
1056	1013	1070	1076	909		948	1079	1001	
977	929	981	925	838	928	916	924	909	CH_2 rock skeletal vibrations
929	854	853	806	814	857	877	813	838	
881	770	752	723	711	769	829		814	C-H out –of plane
	695		695		694	754	694	715	-NO_2 wag vibration
679	647	692	643	651	615	666	642	651	



Scheme 1 shows the optimized structures of (A) TR- PHB, (B) TR- DNBA, (C) TR- MDNB, (D) TR-CAA [Dim grey: Carbon atoms; Light cyan: Hydrogen atoms; Red: Oxygen atoms; Dark Blue: Nitrogen atom; Green: Chlorine atom; Dotted Line: Hydrogen bonding].

The following observations on the spectra of 1H-1,2,4-triazole (TR) with 4-hydroxybenzoic acid (PHB), 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (CAA), 1,3-dinitrobenzene (MDNB) and 3,5-dinitrobenzoic acid (DNBA), were made:

- The carbonyl C = O stretching vibration appearing at 1680cm^{-1} in the IR spectrum of PHB is shifted to 1682 cm^{-1} in the IR of the CT complex of PHB with TR.

- The carbonyl C = O stretching vibration appearing at 1632 cm^{-1} in the IR spectrum of DNBA shifted to 1635 cm^{-1} in IR of the CT complex of DNBA with TR.
- The carbonyl C = O stretching vibration appearing at 1628 cm^{-1} in the IR spectrum of CAA shifted to 1635 cm^{-1} in the IR of the CT complex of CAA with TR.
- The IR Spectra of the formed CT complexes show NH^{+} bands at 2829, 2869, 2821 and 2871 cm^{-1} for TR with PHB, MDNB, DNBA and CAA Complexes confirming the formation of hydrogen bonded proton transfer between OH of PHB, CAA, H atom at the ortho position of two NO_2 of MDNB and DNBA with the ring nitrogen of TR.
- The TR ring vibrations appearing at (1525, 1453, 1378 and 1318) cm^{-1} of the donor TR are shifted to (1599, 1508, 1448 and 1420 cm^{-1}), (1575, 1531, 1436 and 1396 cm^{-1}), (1529, 1501, 1488 and 1410 cm^{-1}) and (1599, 1543, 1416 and 1349) cm^{-1} in the CT of complexes TR with PHB, CAA, MDNB and DNBA respectively [54-55].

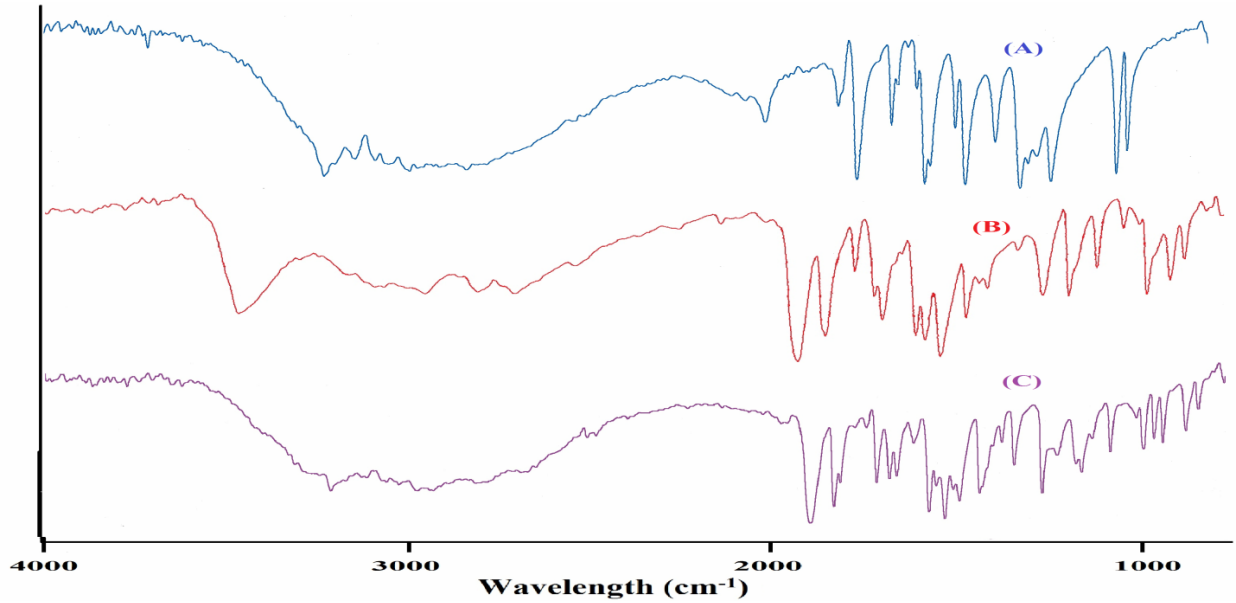


Figure 1: FT- IR of (A) TR; (B) PHB; (C) CT of TR & PHB.

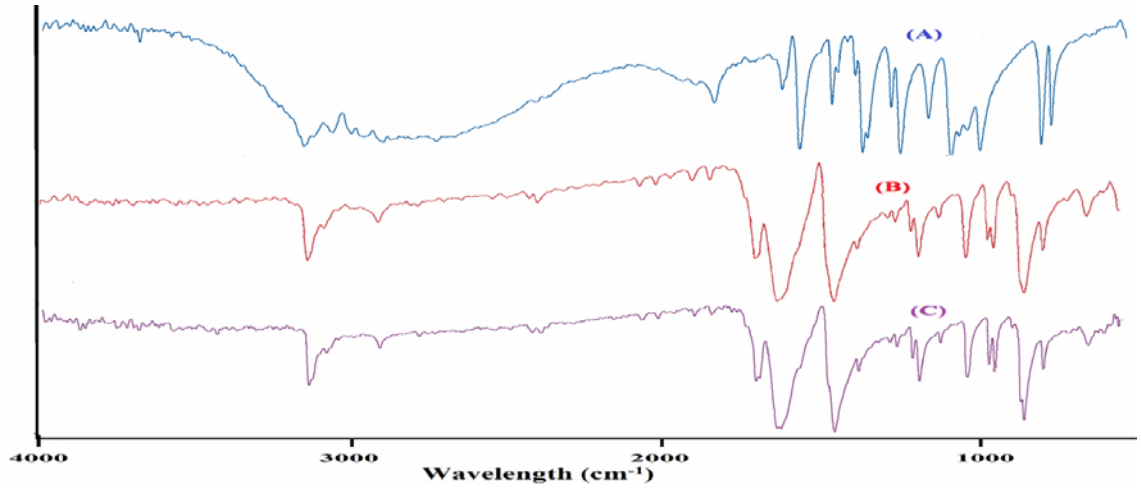


Figure 2: FT- IR of (A) TR; (B) MDNB; (C) CTC of TR & MDNB.

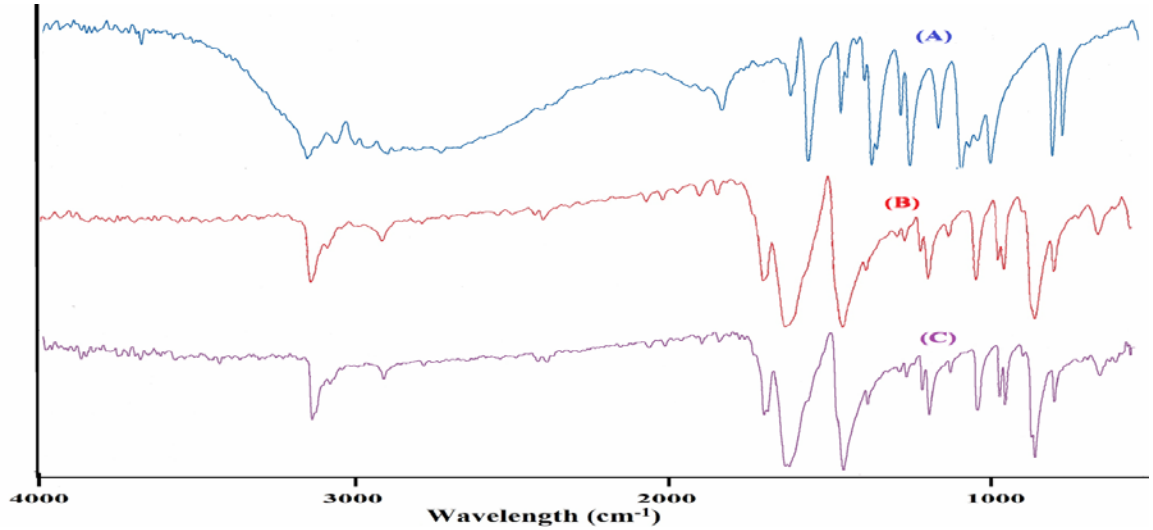


Figure 3: FT- IR of (A) TR; (B) DNBA; (C) CT of TR & DNBA.

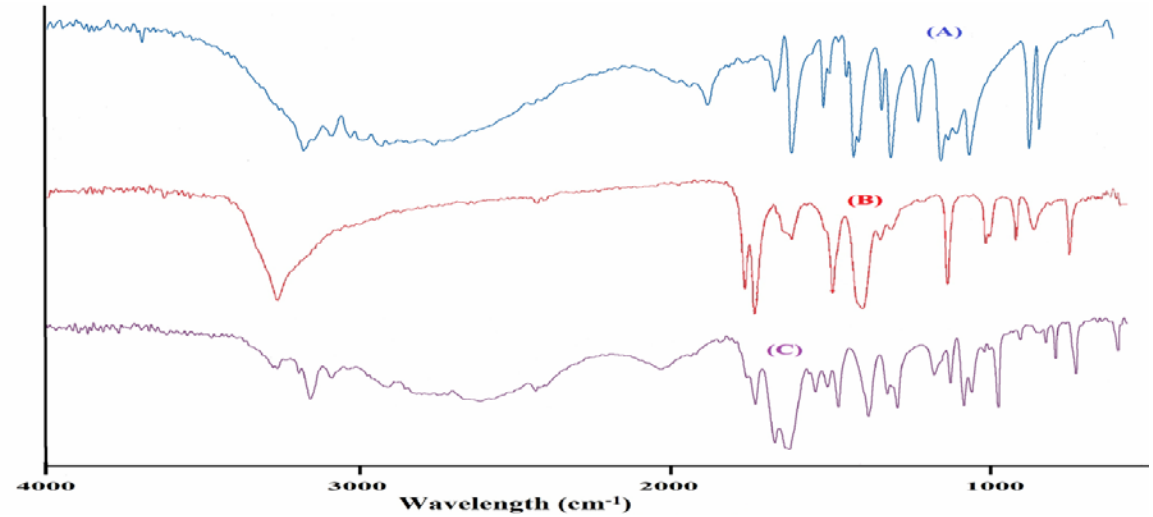


Figure 4: FT- IR of (A) TR; (B) CAA; (C) CTC of TR & CAA.

3.2. Powder X- Ray Diffraction Studies: –

In order to further confirm the crystalline structures of TR- PHB, TR- MDNB, TR- DNBA and TR- CAA, powder X-Ray Diffraction (XRD) measurements were made with X-ray diffraction 179 (Rigaku, Japan, Miniflex-II) using Cu-Kα radiation (λ = 1.5418 Å) in 2θ range from 20º to 80º. 180 The XRD spectra for all reactants and products are shown in Figures 5 to 8. The results are as under

- The XRD spectrum of TR (Figure 5 (A)) gave characteristic peaks at 2θ = 22°, 23°, 25°, 28°, 31°, 37°, 43°, 54°, 78°; PHB (Figure 5 (B)) gave 23°, 25°, 29°, 37° and CTC of TR and PHB (Figure 5 (C)) 21°, 23°, 25°, 29°, 37° and 43° corresponding to the new compound formed and indicating a crystal structure of the TR- PHB complex.
- The XRD spectrum of TR (Figure 6 (A)) gave characteristic peaks at 2θ = 22°, 23°, 25°, 28°, 31°, 37°, 43°, 54°, 78°; MDNB (Figure 6 (B)) gave 24°, 26°, 37°, 44° and CTC of TR and MDNB (Figure 6 (C)) 20°, 22°, 26°, 30°, 38°, 40° and 44° corresponding to the new compound formed and indicating a crystal structure of the TR- MDNB complex.
- The XRD spectrum of TR (Figure 7 (A)) gave characteristic peaks at 2θ = 22°, 23°, 25°, 28°, 31°, 37°, 43°, 54°, 78°; DNBA (Figure 7 (B)) gave 22°, 23°, 24°, 26°, 32°, 38° and CTC of TR and DNBA (Figure 7 (C)) gave peaks at 20°, 23°, 24°, 29°, 31°, 38° and 43° corresponding to the new compound formed and indicating a crystal structure of the TR- DNBA complex.
- The XRD spectrum of TR (Figure 8 (A)) gave characteristic peaks at 2θ = 22°, 23°, 25°, 28°, 31°, 37°, 43°, 54°, 78°; CAA (Figure 8 (B)) gave peaks at 23°, 25°, 27°, 31°, 34°, 39°, 40°, 44° and CTC of TR and CAA (Figure 8 (C)) gave peaks at 8°, 17°, 19°, 23°, 27°, 33° and 36° corresponding the new compound formed and indicating a crystal structure of the TR- CAA complex. [56]

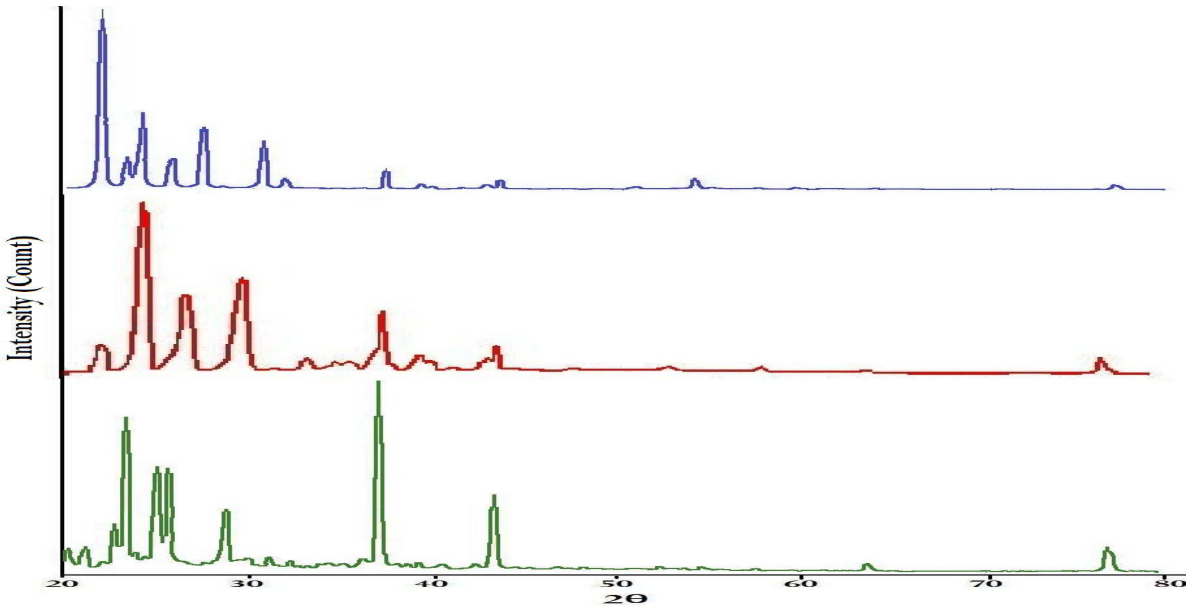


Figure 5: XRD spectrum of (A) TR; (B) PHB; (C) CTC of TR & PHB.

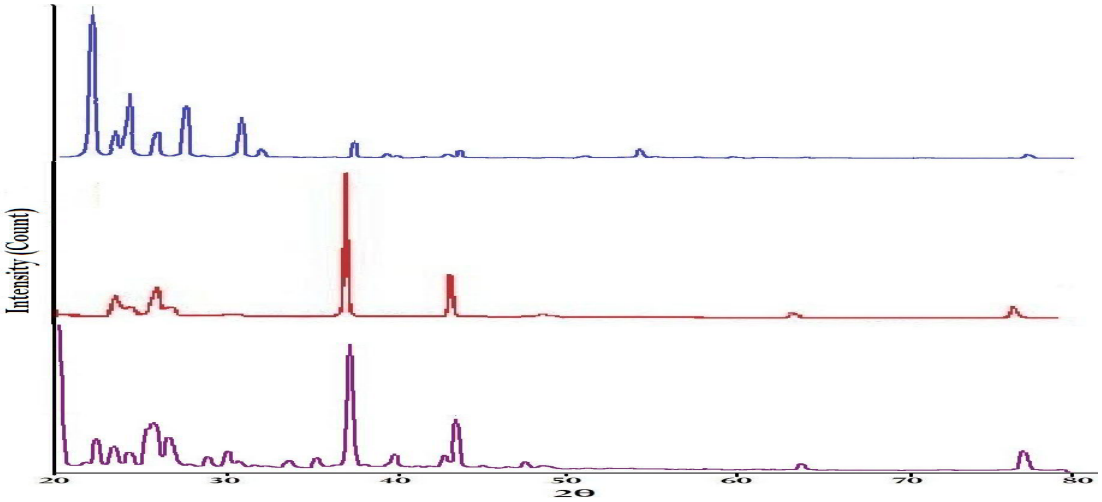


Figure 4.6: XRD spectrum of (A) TR; (B) MDNB; (C) CTC of TR & MDNB.

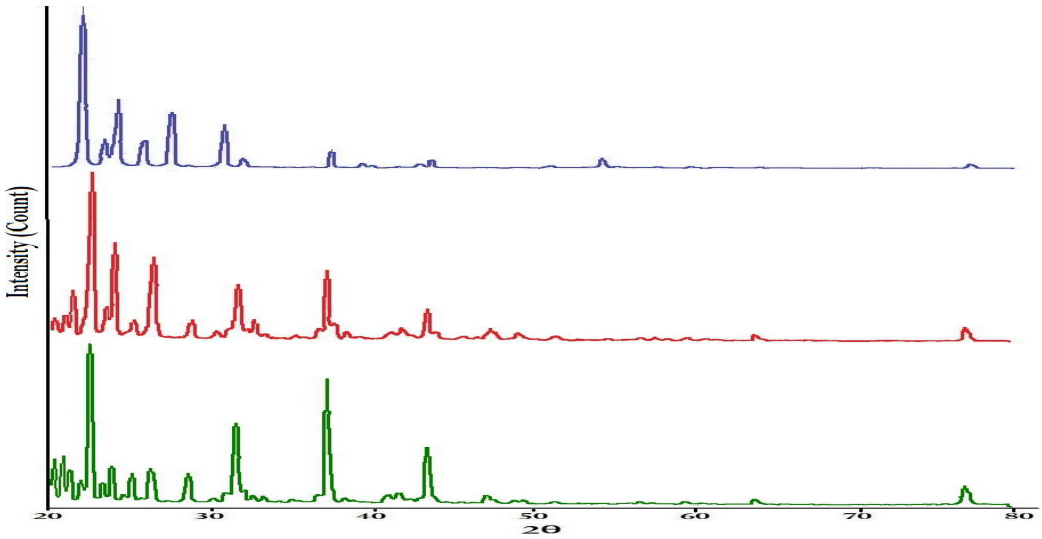


Figure 7: XRD spectrum of (A) TR; (B) DNBA; (C) CTC of TR & DNBA.

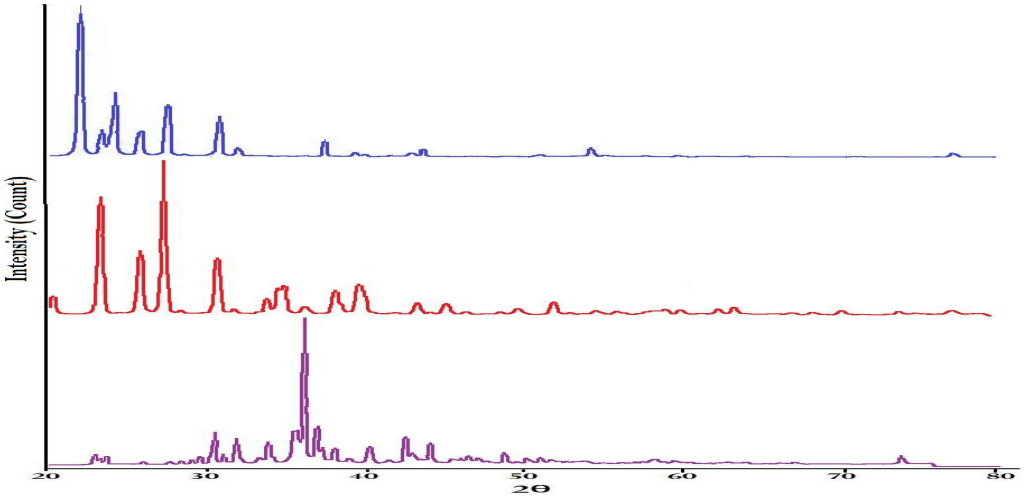


Figure 8: XRD spectrum of (A) TR; (B) CAA; (C) CTC of TR & CAA.

3.3. ^{1}H NMR Measurements: –

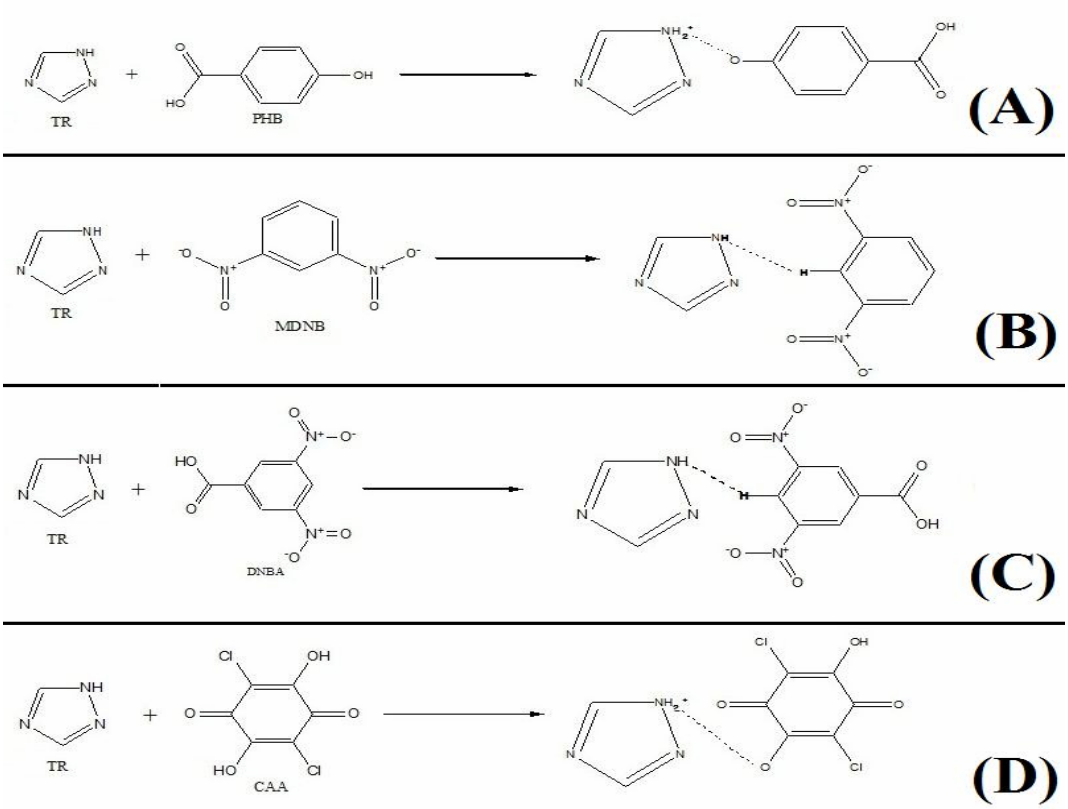
The proton NMR spectra of the reactants and the formed CT complexes were measured in DMSO using Bruker Advance 11 400 NMR spectrometer. The chemical shifts (δ) of different types of CT complex are listed in Table 2 and given in Figures 9 to 12. There are some changes in the chemical shift values of CT complexes rather than the free donor and acceptors in ^{1}H NMR spectrum [57]. In the ^{1}H NMR spectrum of the complexes formed from the interactions between TR as electron donor with π acceptors such as PHB, MDNB, DNBA and CAA, the NH group of the donor makes intermolecular hydrogen bonding with the hydrogen atom at ortho position related to two nitro groups Electron withdrawing (EWD) in MDNB,DNBA which makes that hydrogen more liberate, in PHB with the proton of OH group and may be with proton of COOH group, in CAA with one of the two protons of two OH groups to make intermolecular hydrogen bonding with NH group from the donor .

Table 2: ^{1}H NMR spectral data of TR with PHB, MDNB, DNBA and CAA and their CT complexes.

Compound	**^{1}H NMR chemical shift δ ppm**	**Assignments**
TR	8.2	s; 2H; (1H- TR)
	14.2	br; 1H; (1H- N- TR)
PHB	6.84	d; 2H- Ar
	7.8	d; 2H- Ar
	10.2	br; 1H- Ar- OH
	12.4	br; 1H- Ar- COOH
CTC of TR & PHB	2.0	s; 1H- Ar
	2.5	s; 2H- Ar
	6.8	M; 1H- Ar
	7.8	M; 1H- Ar
	8.2	s; 1H- Ar
	10.1	br; 1H- Ar- COOH
	11.2	br; 2H- Ar- NH-2-TR
MDNB	7.7	d; 1H- Ar
	8.5	d; 1H- Ar
	8.6	d; 1H- Ar
	8.9	s; 1H- Ar
CTC of TR & MDNB	2.1	s; 2H- NH-TR
	2.6	s; 1H- TR
	3.2	s; 1H- TR

	7.9	M; 1H- Ar
	8.2	s; 1H- Ar
	8.6	M; 1H- Ar
DNBA	8.9	s, 2H; 2 (1H- Ar) (in ortho position to COOH)
	9.02	s;1H-Ar (in ortho position to NO_2)
	13.6	br ; 1H(Ar-COOH)
CTC of TR & DNBA	2.1	s; 1H –NH –Ar-TR
	2.5	d;1H- Ar
	8.0	s; 1H- Ar
	9.0	d; 2H- Ar
	9.1	T; 1H- Ar
	11.1	br; 1H- Ar- COOH
CAA	6.1	br; (1H- Ar)
	8.0	s; (1H- Ar)
CTC of TR & CAA	2.1	s; 2H-NH_2- Ar-TR
	5.4	br; 1H-TR
	8.2	s; 1H-TR
	8.5	s; 1H-Ar

The previous results coincide with the FT- IR Spectra results. Consequently, one concludes that the molecular complexes between TR and the studied acceptors are formed through electron and proton transfer that can be formed. The aromatic protons in TR, CAA, and DNBA were assigned following the previously known data in the literature [58] in the regions 2 to 2.6 ppm, while the phenolic protons of PHB were assigned at 11.2 ppm. The ^{1}H NMR spectra of the complexes reveal several observations. All the observed peaks in the spectra of the individual components are also present in the complexes' spectra suggesting their formation. The proton signals of the donor TR are shifted downfield to higher ppm values indicating a charge migration from the donor towards the acceptors. The ^{1}H NMR signal due to the phenolic protons in two acceptors (CAA, PHB) disappeared in the complexes spectra indicating deprotonation and in the MDNB a new peak is observed in the complexes spectra in the region 2 to 3 ppm and assigned to N^+–*H* protons indicating protonation of the donor TR, suggesting that the interaction of TR as a donor with PHB, CAA, DNBA and MDNB in a molar ratio of 1:1 according to the following equations in Scheme 2.



Scheme 2 shows the reaction and the intermolecular hydrogen bonding between (A) TR & PHB; (B) TR & MDNB; (C) TR & DNBA; (D) TR & CAA.

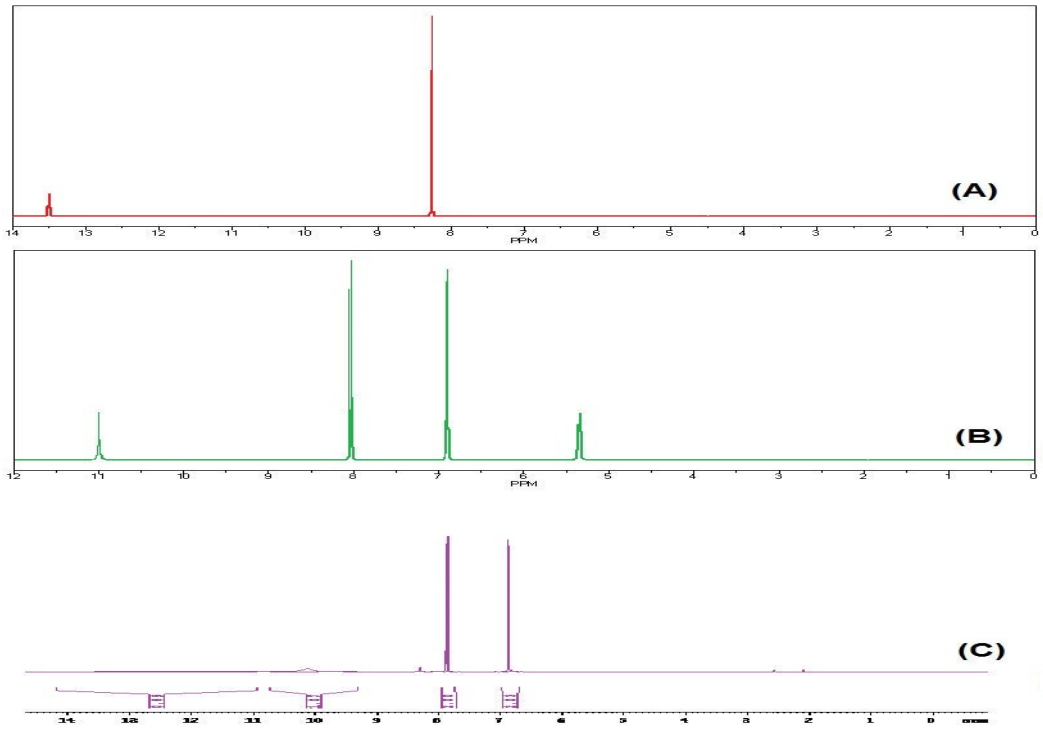


Figure 9: ^{1}H NMR of (A) TR; (B) PHB; (C) CTC of TR & PHB.

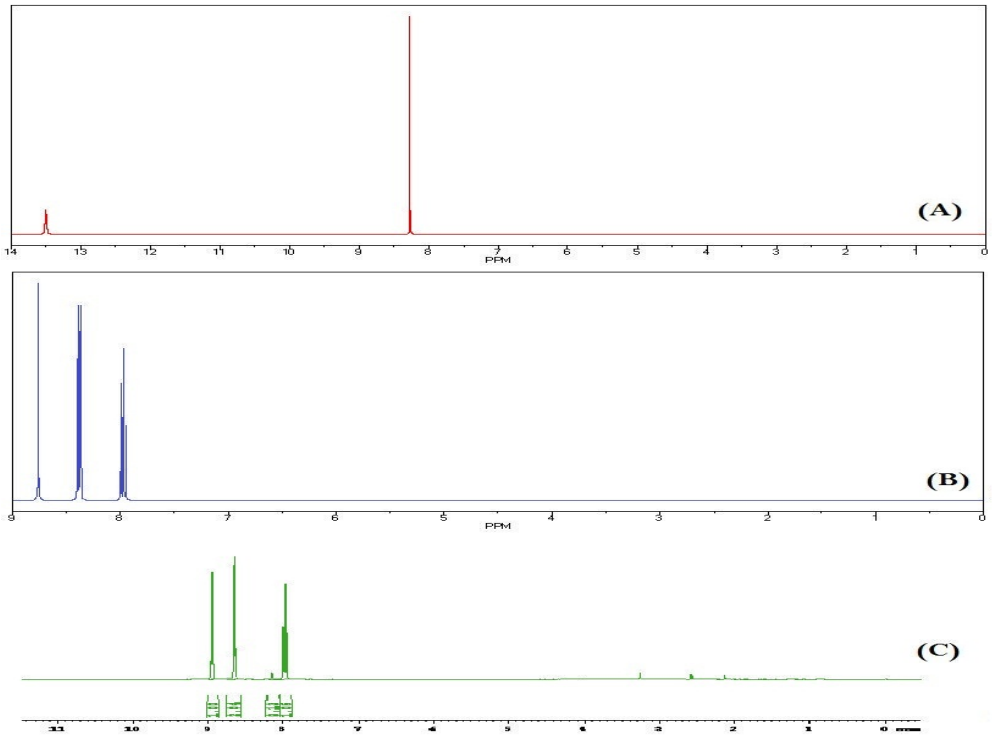


Figure 10: ^{1}H NMR of (A) TR; (B) MDNB; (C) CTC of TR & MDNB.

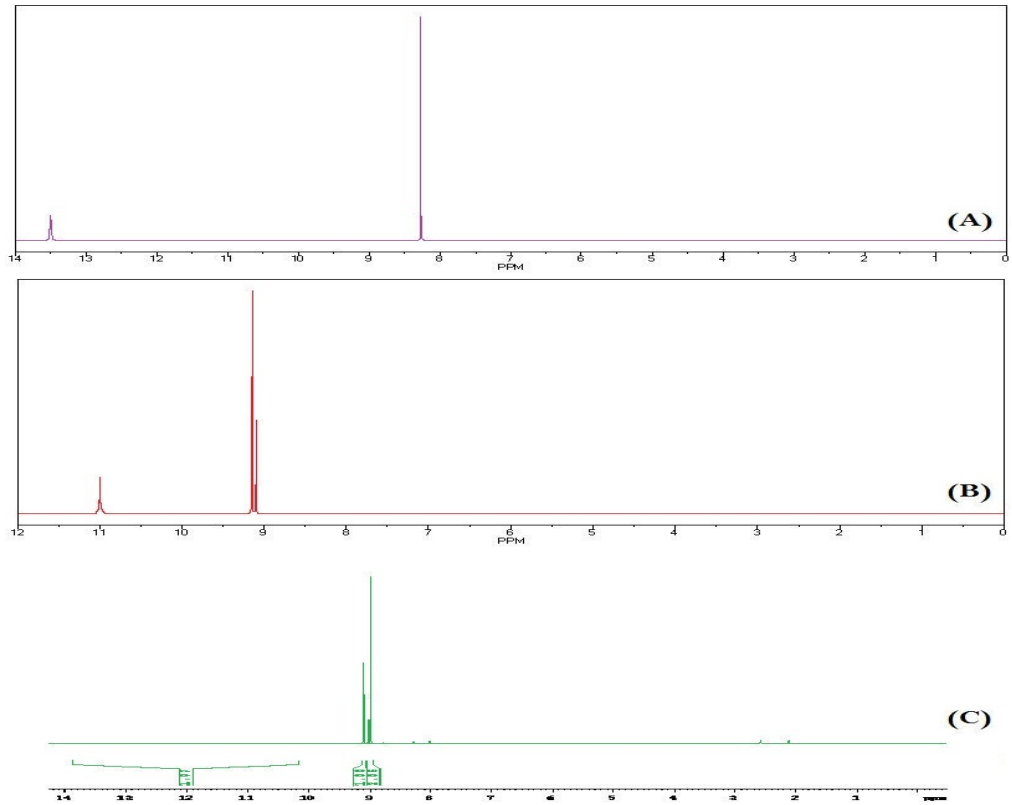


Figure 11: ^{1}H NMR of (A) TR; (B) DNBA; (C) CTC of TR & DNBA.

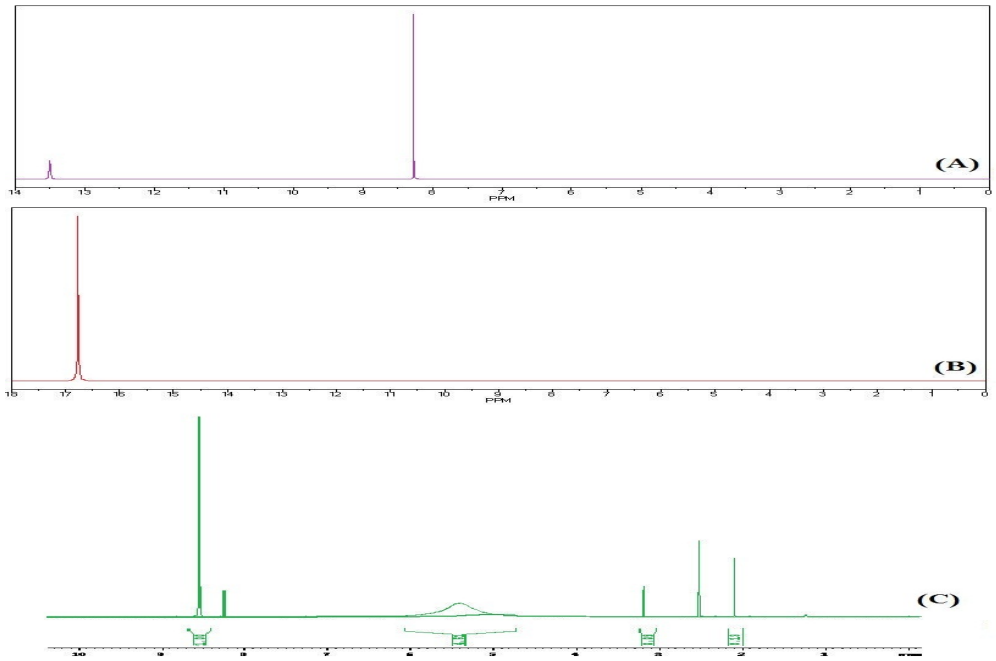


Figure 12: ^{1}H NMR of (A) TR; (B) CAA; (C) CTC of TR & CAA.

3.4. Conductivity Measurements:

The conductivity of TR (0.01, 0.02 and 0.03, 0.04, 0.05 mol L^{-1}) with 0.01 mol.L^{-1} acceptors from PHB, MDNB, DNBA and CAA in methanol and acetone obtained by Systronics Conductivity meter 306 Ahmadabad. By plotting the different concentrations of the donors against the conductivity at 30.0 °C, it was found to be a straight line with increasing concentration. It is evident from Table 3 and Figure 13, that the conductivity of 0.01 TR in methanol equals 8.9µS, but when we mixed it with 0.01 M PHB, the conductivity become 8.5µS and, when increasing the concentration of TR and keeping the concentration of PHB constant at 0.01 M, the conductivity increase to 16.1 µS (at concentration of donor 0.05 M). This occurs in all the mixings between TR with MDNB, DNBA and CAA (Formation of CTC in solution). It is also clear from Figure 14, that the conductivity of 0.01 TR in acetone equals to 7.9 µS and this is 1ess than the similar concentration of TR in methanol. But, when we mixed it with 0.01 M PHB, the conductivity become, 10.7 µS, with increasing the concentration of TR and keeping the concentration of PHB constant at 0.01 M, the conductivity become, 18.6 µS (at concentration of donor 0.05M). This occurs in all the mixings between TR with MDNB, DNBA and CAA.

Table 3: The conductivity and molar conductance of TR with PHB, DNBA, MDNB and CAA in different solvents at 30°C.

Compound	[A] :[D]	Conductivity (µS) in MeOH	Conductivity (µS) in acetone
TR	0.01 M	8.9	7.9
CTC of TR & PHB	0.01 M : 0.01 M	8.5	10.7
	0.01 M : 0.02 M	10.4	12.6
	0.01 M : 0.03 M	12.2	14.5
	0.01 M : 0.04 M	14.1	15.7
	0.01 M : 0.05 M	16.1	18.6
CTC of TR & DNBA	0.01 M : 0.01 M	15.6	27.5
	0.01 M : 0.02 M	17.6	29.6
	0.01 M : 0.03 M	19.5	31.5
	0.01 M : 0.04 M	21.6	34
	0.01 M : 0.05 M	23.4	36.3
CTC of TR & MDNB	0.01 M : 0.01 M	10.1	9.9
	0.01M : 0.02 M	11.9	11.7
	0.01 M : 0.03 M	13.7	13.3
	0.01 M : 0.04 M	15.7	14.3
	0.01 M : 0.05 M	17.6	16.8
CTC of TR & CAA	0.01 M : 0.01 M	13.5	13.1
	0.01M : 0.02 M	15.6	19.3
	0.01 M : 0.03 M	17.8	25.3
	0.01 M : 0.04 M	19.7	32.1
	0.01 M : 0.05 M	21.4	37.3

The resulting donor–acceptor solutions in methanol and in acetone exhibit appreciable conductivity which may be explained by the possible formation of charge transfer complexes between the reaction of donor and acceptor in solution [59-61]. It has been observed that the conductivity of charge transfer complexes in solvent increase with an increase in polarity of the solution and with increasing the concentration of donor and depends on the type on the donor and the acceptor. This is shown in Table 3. Moreover, the increase in conductivity is due to the fact that the dative structure D^+ -A^- should be stabilized in less polar solvent [62]. We obtained that the molar conductance decreases with increase in the concentration of the solution.

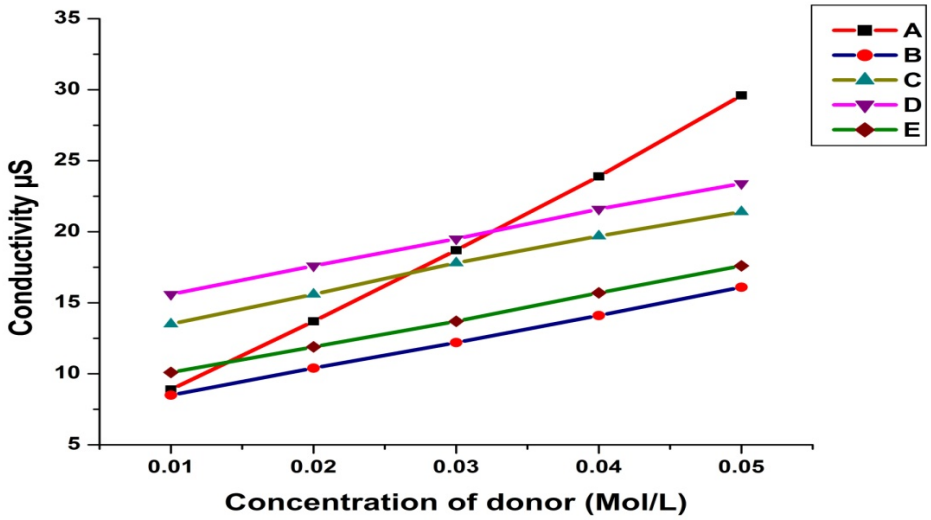


Figure 13:- Plot of the conductivity and the concentration of the donor in solution (A) TR (B) TR- PHB (C) TR- CAA (D) TR- DNBA (E) TR- MDNB in methanol.

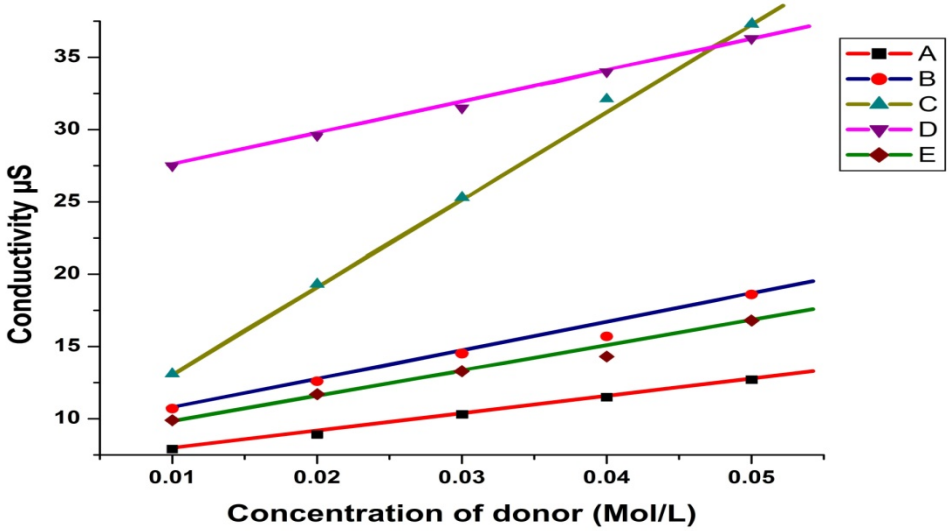


Figure 14:- Plot of the conductivity and the concentration of the donor in solution (A) TR (B) TR-PHB (C) TR-CAA (D) TR-DNBA (E) TR-MDNB in acetone.

3.5. Fluorescence Studies

Fluorescence spectra were recorded at room temperature (35%) in acetone in the range of 300-750 nm, using an excitation 250 nm. It was observed that the acceptors (PHB, MDNB, DNBA and CAA) quenched the emission of fluorescence of the donor (TR) through the formation of charge transfer complexes.

The fluorescence changing is usually classified as dynamic quenching and static quenching [63]. Dynamic quenching results from collision between flurophore and quencher whereas static quenching is due to ground state complex formation between flurophore and quencher. The binding of TR with some

acceptors where studied in the intrinsic fluorescence of CTC at different concentration of donor in the Figures 15-18.

The experimental results indicate that the quenching efficiency depends on the type of the acceptor and the concentration of the donor. From Figure 15 of the CTC of TR and PHB, we obtain that the intensity of emission of CTC of 0.01 M TR with 0.01 M PHB (3ml) is 175 but after increasing the concentration of TR to 0.04 M, the intensity of emission decreases to 37. (Ratio 1:4).

From Figure 16, we obtain that the intensity of emission of CTC of 0.01 M TR with 0.01 M MDNB is 325 but after changing the concentration of TR to 0.04 M, it becomes 45 at a fixed concentration of the acceptor (Ratio 1:4).

From Figure 17, we obtain that the intensity of emission of CTC of 0.01 M TR with 0.01 M DNBA is 225 but it becomes 70 at 0.04 M TR with a fixed concentration of DNBA (0.01M) (Ratio 1:4).

From Figure 18, we obtain that the intensity of CTC of 0.01 M TR with 0.01 M CAA equals to 165 and it decreases to 63 at 0.04 M TR with 0.01M CAA (at donor acceptor ratio of 1:4).

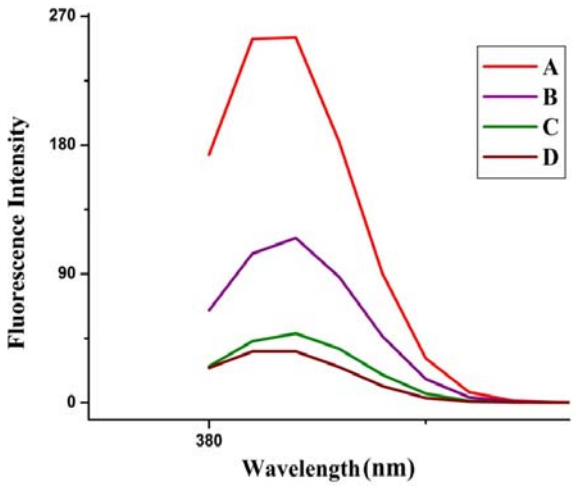


Figure 15: Fluorescence spectra of 0.01 M -0.04 M with 0.01 M PHB.

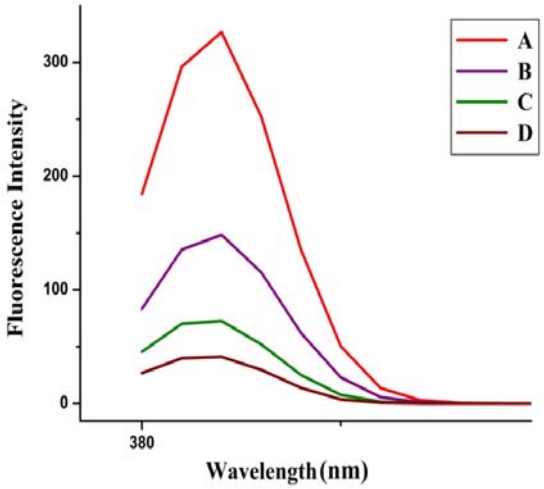


Figure 16: Fluorescence spectra of 0.01 M - TR 0.04 M TR with 0.01 M MDNB.

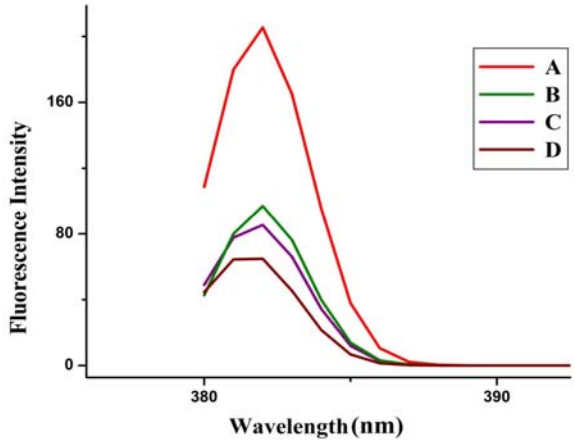


Figure 17: Fluorescence spectra of 0.01 M -0.04 M TR with 0.01 M DNBA.

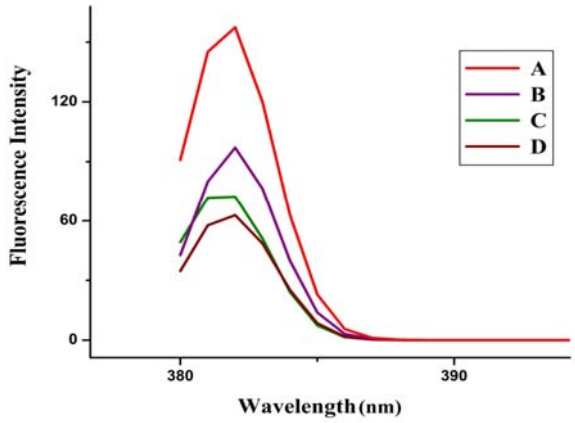


Figure 18: Fluorescence spectra of 0.01M -0.04M TR with 0.01 M CAA.

4. Conclusions

The ^{1}H NMR for the study of CTC of 4-hydroxybenzoic acid (PHB), 1,3-dinitrobenzene (MDNB), 3,5-dinitrobenzoic acid (DNBA) and 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (CAA) with 1H-1,2,4-triazole (TR) reveals that it forms 1:1 hydrogen- bonding network between the aromatic donor and acceptors in its crystal structure due to transfer of proton of acceptors moiety to the donor moiety ($–NH^{+}$). The interaction between the donor and acceptor was bonded proton-transfer complex of 1H-1,2,4-triazole (TR) with 4-hydroxybenzoic acid (PHB), 1,3-dinitrobenzene (MDNB), 3,5-dinitrobenzoic acid (DNBA) and 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (CAA) has been attributed to extensive and found to be π-π* transitions by the formation of radical ion pairs. The FT-IR spectrum shows that the complex formed between donor and acceptor by transferring a proton from acceptors 4-hydroxybenzoic acid (PHB), 1,3-dinitrobenzene (MDNB), 3,5-dinitrobenzoic acid (DNBA) and 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (CAA) to the donor 1H-1,2,4-triazole (TR). The XRD spectrum shows that the CT complexes for D & A obtained new bands corresponding to new compounds form and indicating crystal structures of TR– PHB, TR– MDNB, TR–DNBA, TR– CAA. From the data and graphs of conductivity, we obtain that the conductivity increases with increasing the concentration of the donor and it depends on the polarity of the solution and the type of the acceptor. We also observed that the molar conductance decreases with the increasing concentration of the solution. The physical results (melting point and solubility of reactant and products in different solvents) clearly indicate that the products of the reactions seem to be new compounds that have chemical and physical behavior that is different from the reactants. The fluorescence spectrum of the CT Complexes shows that the intensity of emission decreases with increase in the concentration of the donor.

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