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Electronic, infrared, and ^{1}HNMR spectral studies of the novel charge-transfer complexes of *o*-tolidine and *p*-toluidine with alternation π-acceptors (3,5-dinitro benzoic acid and 2,6-dichloroquinone-4-chloroimide) in $CHCl_3$ solvent

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Abstract

The rapid interaction between *o*-tolidine and *p*-toluidine (π-donors) with the π-acceptors, e.g., 3,5-dinitrobenzoic acid (DNB) and 2,6-dichloroquinone-4-chloroimide (DCQ) results in the formation of 1:1 charge-transfer complexes as the final products, [(*o*-tolidine) (acceptor)] and [(*p*-toluidine) (acceptor)]. The final products of the reactions have been isolated and characterized using FTIR, ^{1}HNMR spectroscopy and elemental analysis as well as photometric titration. The stoichiometry and apparent formation constants of the complexes formed were determined by applying the conventional spectrophotometric molar ratio method.

Keywords: Charge-transfer; *o*-Tolidine; *p*-Toluidine; 2,6-Dichloroquinone-4-chloroimide; ^{1}HNMR spectra

1. Introduction

Many of the electron donor–acceptor (EDA) interactions had been widely studied spectrophotometrically in the determination of drugs that are easy to be determined based on CT-complex formation with some electron acceptors. 2,6-Dichloroquinone-4-chloroimide (DCQ, Gibbs reagent), 7,7′,8,8′-tetracyanoquinodimethane (TCNQ), *p*-chloranil (CL) and chloranilic acid (CLA) are strong π-acceptors drugs and the review of literature in the last decade have been mainly concentrated on the CT-complexes spectral studies [1–5]. A vast number of the charge-transfer complexes formed during the reaction of σ- and π-acceptors with organic compounds containing different sites of donation (nitrogen, oxygen, or sulfur atoms) were extensively investigated [6–10]. This paper is a continuation of our previous investigation [11–14] concerned with the formation of stable charge-transfer complexes formed during the reaction of electron donors (nickel(II) and Fe(III) acetylacetonates, polyamido-amine dendrimers 1,8-naphthalimide polyamidoamine (PAM1) and 4-piperidino-1,8-naphthalimide polyamidoamine (PAM2), benzanthrone derivatives) with iodine and different π-acceptors like DDQ, TCNQ, and *p*-chloranil.

The present investigation tends to elucidate mainly the study of the reactions of both 3,5-dinitrobenzoic acid (DNB) and 2,6-dichloro quinone-4-chloroimide (DCQ) (π-acceptors) for the first time with *o*-tolidine and *p*-toluidine (electron donors) and interpreting the nature of these interactions using ^{1}HNMR, IR-spectral, electronic absorption as well as elemental analysis data.

2. Experimental

Reagent grade chemicals were used throughout. *p*-Toluidine and 2,6-dichloroquinone-4-chloroimide were obtained from Merck Chemical Co., while *o*-tolidine and 3,5-dinitrobenzoic acid were obtained from Aldrich Chemical Co.

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2.1. Analysis and physical measurements

Electronic spectra were recorded at room temperature via both Shimadzu UV-Spectrophotometer model 1601 PC with quartz cell of 1 cm path length and Jenway 6405 Spectrophotometer each for certain reactions. IR-spectra, as KBr discs, were recorded on a Gensis II FT-IR spectrophotometer (400–4000 cm^{-1}). ^{1}HNMR spectra in dmso-d_6 were measured on a Varian Gemini 200 MHz Spectrometer using TMS as an internal standard. Microanalysis for carbon, hydrogen, nitrogen, and chloride were carried out at the Micro analytical centers, Cairo University, Cairo, Egypt using a Perkin-Elmer CHN 2400.

2.2. Photometric measurements

The photometric titration measurements were carried out within the reactions between the acceptors (DCQ and DNB) and the two donors (*o*-tolidine and *p*-toluidine) in $CHCl_3$ at 20 °C. The concentration of the two donors in the reactions mixtures were kept fixed (1.0×10^{-4} M) while the concentration of the acceptors DCQ and DNB changed over a wide range of concentrations (0.25×10^{-4} to 3.0×10^{-4} M) to produce solution in each case of acceptor: donor molar ratio varying from 1.0:0.25 to 1.0:3.0. The peak absorbance of the resulted CT-complexes at 301 nm for [(*o*-tolidine) (DCQ)], 249 and 291 nm for [(*o*-tolidine) (DNB)], 245 and 270 nm for [(*p*-toluidine) (DCQ)], and 290 nm for [(*p*-toluidine) (DNB)] were measured for each reaction mixture and plotted as a function of the two acceptors (DCQ or DNB) to two donors (*o*-tolidine or *p*-toluidine) molar ratio. The stoichiometry of the molecular CT-complexes under investigation were determined by the application of the conventional spectrophotometric molar ratio according to the known methods [15] and were also used to obtain the modified Benesi–Hildebrand plots [16–18] in order to calculate the formation constant, *K*, and the absorpativity, ε, values for each CT-complexes resulted from this study.

2.3. Preparation and characterization of the CT-complexes

IR, ^{1}HNMR, and electronic UV–vis spectroscopy, as well as micro analytical analyses elucidated structures of the formation of CT-complexes reported in this study. The results of the elemental analyses (%, yield), (mp, °C), and color are given in Table 1.

2.4. [(*o*-Tolidine) (DCQ)] (*1*) and [(*p*-toluidine) (DCQ)] (*3*)

A brown solution of the 2,6-dichloroquinone-4-chloroimide (DCQ, acceptor) (0.841 g, 4 mmol) in C_2H_5OH (25 ml) was added at room temperature to each of the two colorless solutions (two donors) of *o*-tolidine (0.212 g, 1 mmol) and *p*-toluidine (0.107 g, 1 mmol) in C_2H_5OH (15 ml) and then stirred for about 15 min. The dark brown (complex **1**) and dark green (complex **3**) precipitates formed were filtered off, washed with the diethyl ether (3 ml) and dried in vacuum over $CaCl_2$.

2.5. [(*o*-Tolidine) (DNB)] (*2*) and [(*p*-toluidine) (DNB)] (*4*)

To the two solutions of *o*-tolidine (0.212 g, 1 mmol) and *p*-toluidine (0.107 g, 1 mmol) in $CHCl_3$ (15 ml), a saturated solution of 3,5-dinitrobenzoic acid (0.636 g, 3 mmol) in $CHCl_3$ (50 ml) was added (to each mentioned donor). The two novel orange colored CT-complexes for each donor (*o*-tolidine or *p*-toluidine) resulted were filtered off, washed with $CHCl_3$ (5 ml) and dried in vacuum over $CaCl_2$.

3. Results and discussion

The electronic absorption spectra (UV–vis) of the donors, *o*-tolidine and *p*-toluidine (1.0×10^{-4} M) with different electron π-acceptors (2,6-dichloroquinone-4-chloroimide and 3,5-dinitro benzoic acid (1.0×10^{-4} M) under investigation in chloroform solution show an extra absorption band not due to any one of the components alone (Fig. 1). Furthermore, neither electron donors nor electron acceptors is absorbed in the region of absorption of the molecular complexes formed. These bands have been attributed to the formation of donor–acceptor molecular complexes in these solutions. The CT-absorption bands represented in the spectra due to the resulted CT-complexes were appeared at 301 nm (very strong band, hyperchromic effect) for [(*o*-tolidine) (DCQ)] (**1**), at 249 and 291 nm for [(*o*-tolidine) (DNB)] (**2**), at 245 and 270 nm for [(*p*-toluidine) (DCQ)] (**3**) (hyperchromic effect

Table 1
Analytical and physical data of [(*o*-tolidine) (DCQ)] (**1**), [(*o*-tolidine) (DNB)] (**2**), [(*p*-toluidine) (DCQ)] (**3**), and [(*p*-toluidine) (DNB)] (**4**) CT-complexes

Compound, MF (M_W)	Elemental analyses, %found (calculated)				Color	Yield (%)	mp (°C)
	C	H	N	Cl			
$C_{20}H_{18}N_3OCl_3$ (**1**) (422.74)	56.24 (56.77)	4.19 (4.25)	9.72 (9.93)	24.97 (25.19)	Dark brown	67	167
$C_{21}H_{20}N_4O_6$ (**2**) (424.41)	59.17 (59.37)	4.63 (4.71)	13.08 (13.19)	–	Orange	89	138
$C_{13}H_{11}N_2OCl_3$ (**3**) (317.61)	48.98 (49.11)	3.40 (3.46)	8.75 (8.81)	33.27 (33.53)	Dark green	91	173
$C_{14}H_{13}N_3O_6$ (**4**) (319.28)	52.44 (52.61)	3.97 (4.07)	13.05 (13.15)	–	Orange	77	134

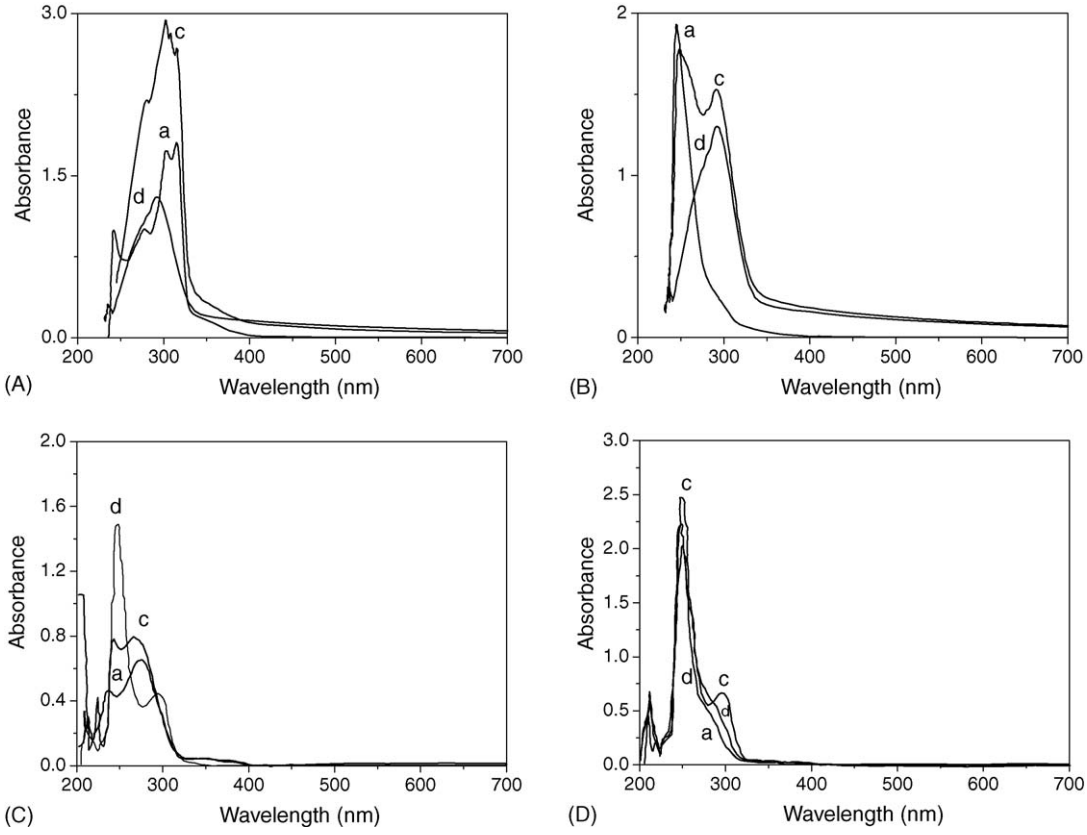


Fig. 1. Electronic absorption spectra of (A) [(*o*-Tolidine) (DCQ)] reaction in $CHCl_3$; (B) [(*o*-tolidine) (DNB)] reaction in $CHCl_3$; (C) [(*p*-toluidine) (DCQ)] reaction in $CHCl_3$; (D) [(*p*-toluidine) (DNB)] reaction in $CHCl_3$. d, donor (1×10^{-4} M); a, acceptor (1×10^{-4} M); c, donor–acceptor CT-complex.

for two bands and noted that the main peak at 245 nm for *p*-toluidine have been reduced (hypochromic effect)) and at 290 nm for [(*p*-toluidine) (DNB)] (**4**). The stoichiometry of the [(*o*-tolidine) (acceptor)] and [(*p*-toluidine) (acceptor)] (where acceptor = 2,6-dichloro quinone-4-chloroimide or 3,5-dinitrobezoic acid) reactions were shown in all cases to be of ratio 1:1. This was concluded according to the obtained elemental analysis data of the isolated solid CT-complexes as indicated in the experimental section, as well as from the complexes infrared spectra, which indicate the existence of the bands which characterize both the donors and the two acceptors. The stoichiometry of 1:1 is also strongly supported by photometric titration measurements. These measurements were based on detected bands at 301 nm for [(*o*-tolidine) (DCQ)] (**1**); at 249 and 291 nm for [(*o*-tolidine) (DCQ)] (**2**); at 245 and 270 nm for [(*p*-toluidine) (DCQ)] (**3**); at 290 nm for [(*p*-toluidine) (DNB)] (**4**). In these measurements, concentration of *o*-tolidine and *p*-toluidine was kept fixed, while the concentration of the acceptors (at the same) were varied over the range of 0.25×10^{-4} to 3.00×10^{-4} M as illustrated in Section 2. Photometric titration curves based on these measurements are shown in Fig. 2. The base-acceptors equivalence points indicate that the ratio in all cases is 1:1 and this result agrees quite well with the elemental analysis, ^{1}HNMR, and infrared spectra of the solid CT-complexes. Accordingly, the formed CT-complexes upon the reaction of *o*-tolidine or *p*-toluidine as donors with the π-acceptors under investigation in $CHCl_3$ have the general formula [(*o*-tolidine) (DCQ)], [(*o*-tolidine) (DNB)], [(*p*-toluidine) (DCQ)] and [(*p*-toluidine) (DNB)]. The 1:1 modified Benesi–Hildebrand Eq. (1) [16–18] was used in the calculations the values of the equilibrium constant, *K*, and the absorpativity, *ε*.

$$\frac{C_a^0 C_d^0 L}{A} = \frac{1}{K\varepsilon} + \frac{C_a^0 C_d^0}{\varepsilon} \tag{1}$$

C_a^0 and C_d^0 are initial concentration of the π-acceptors (DCQ and DNB) and the donors (*o*-tolidine and *p*-toluidine), respectively, whereas *L* refers to optical path length of the cell, while *A* is the absorbance of the illustrated bands for the four new CT-complexes described in this study. The data obtained throughout these calculation are translated by plotting the values of $C_a^0 \times C_d^0/A$ against $C_a^0 + C_d^0$ values for each donor with each acceptor, straight lines are obtained with a slope of $1/\varepsilon$ and intercept of $1/K\varepsilon$ as shown in Fig. 3, for the reactions of two donors in exchange with DCQ and DNB in $CHCl_3$. The values of the *K*, *ε*, and transition energy, E_{CT} associated with these complexes [(*o*-tolidine) (acceptor)] and [(*p*-toluidine) (acceptor)] are given in Table 2. These high

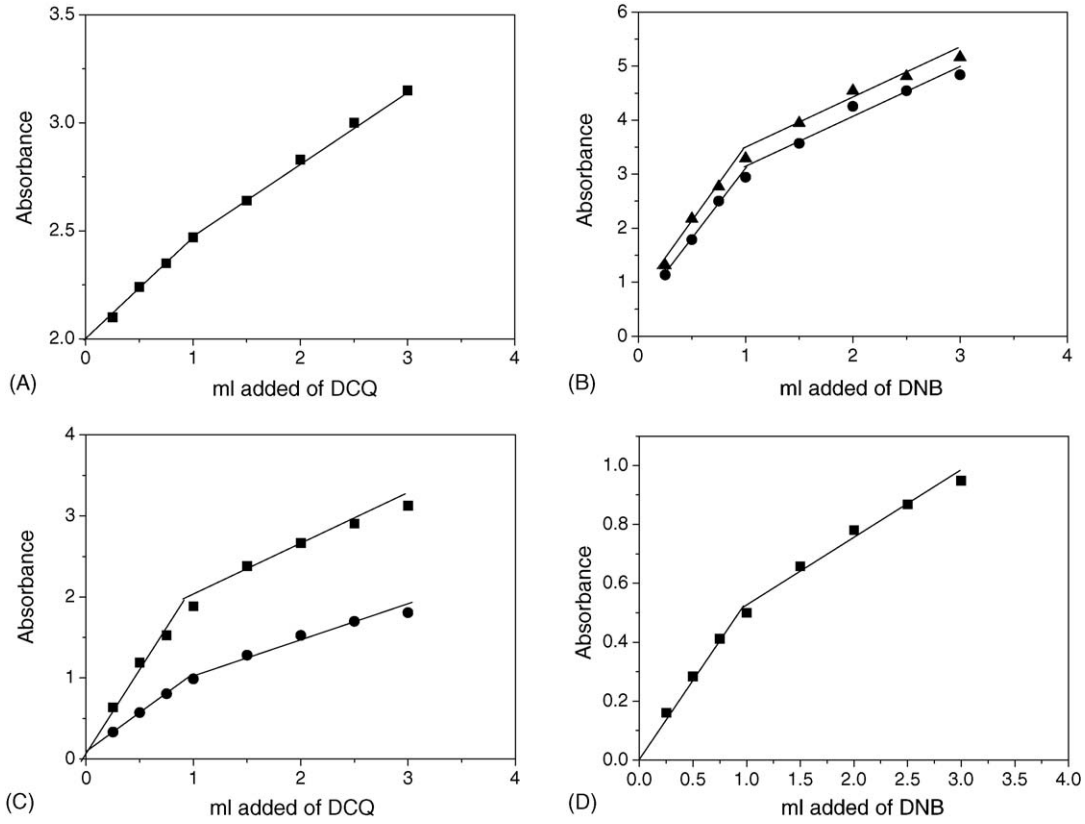


Fig. 2. Photometric titration curves for the donor–acceptor reactions in $CHCl_3$. (A) [(*o*-Tolidine) (DCQ)] reaction at 301 nm; (B) [(*o*-tolidine) (DNB)] reaction at 249 and 291 nm; (C) [(*p*-toluidine) (DCQ)] reaction at 245 and 270 nm; (D) [(*p*-toluidine) (DNB)] reaction at 290 nm.

values of *K* confirm the expected high stabilities of the formed CT-complexes as a result from the expected high donation of the donors (*o*-tolidine and *p*-toluidine). The *K* values obtained are listed in Table 2. When examining the results given in Table 2, it is evident that the order of increasing the stability of the 1:1 intermolecular charge-transfer complexes formed varies depending on the nature of the electron donor and acceptor compounds including the type of electron withdrawing substitutes such as halo and nitro groups according to the following sequence: [(*o*-tolidine) (DCQ)] > [(*o*-tolidine) (DNB)] > [(*p*-toluidine) (DCQ)] > [(*p*-toluidine) (DNB)].

Consequently, the high values of the stability (*K*) for these CT-complexes resulted above can be interpreted as follows: the ground state of the charge-transfer complexes under investigation has no-bond structure, while the excited state has predominantly a dative structure i.e. the structure D^+–A^-. This supports the idea that this dative structure is ionic intermediate [D^+A^-]. Such spectral features (Fig. 1) are in agreement with those reported before for the DDQ^- (DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone) radical ion [19].

The mid infrared spectra of the *o*-tolidine, *p*-toluidine, DCQ, DNB, [(*o*-tolidine) (DCQ)], [(*o*-tolidine) (DNB)], [(*p*-toluidine) (DCQ)] and [(*p*-toluidine) (DNB)] are shown in (Fig. 4) while their band assignments are given in Table 3. If we looked comprehensively, for the first time at the IR-Figures (Fig. 4) for donors, acceptors, and CT-complexes that result from the interaction between the donors and acceptors, we find out that the peaks have shifted to the lower or higher wavenumbers. We could observe also that the peaks of CT-complexes have decreased in intensity. This supports the complexation between the donors and acceptors.

Table 2
Maximum absorption wavelengths λ_{max} (nm), absorpativity ε_{max} (l mole^{-1} cm^{-1}), transition energies (Kcal mole^{-1}) and formation constants *K* (l mole^{-1}) of molecular CT-complexes formed in $CHCl_3$

CT-complexes	λ_{max} (nm)	ε_{max} (l mole^{-1} cm^{-1})	*K* (l mole^{-1})	E_{CT} (kcal mole^{-1})
[(*o*-Tolidine) (DCQ)]	301	3.61×10^4	2.57×10^4	95.00
[(*o*-Tolidine) (DNB)]	291	7.27×10^4	0.647×10^4	98.27
[(*p*-Toluidine) (DCQ)]	270	2.83×10^4	0.545×10^4	105.91
[(*p*-Toluidine) (DNB)]	290	1.70×10^4	0.417×10^4	98.61

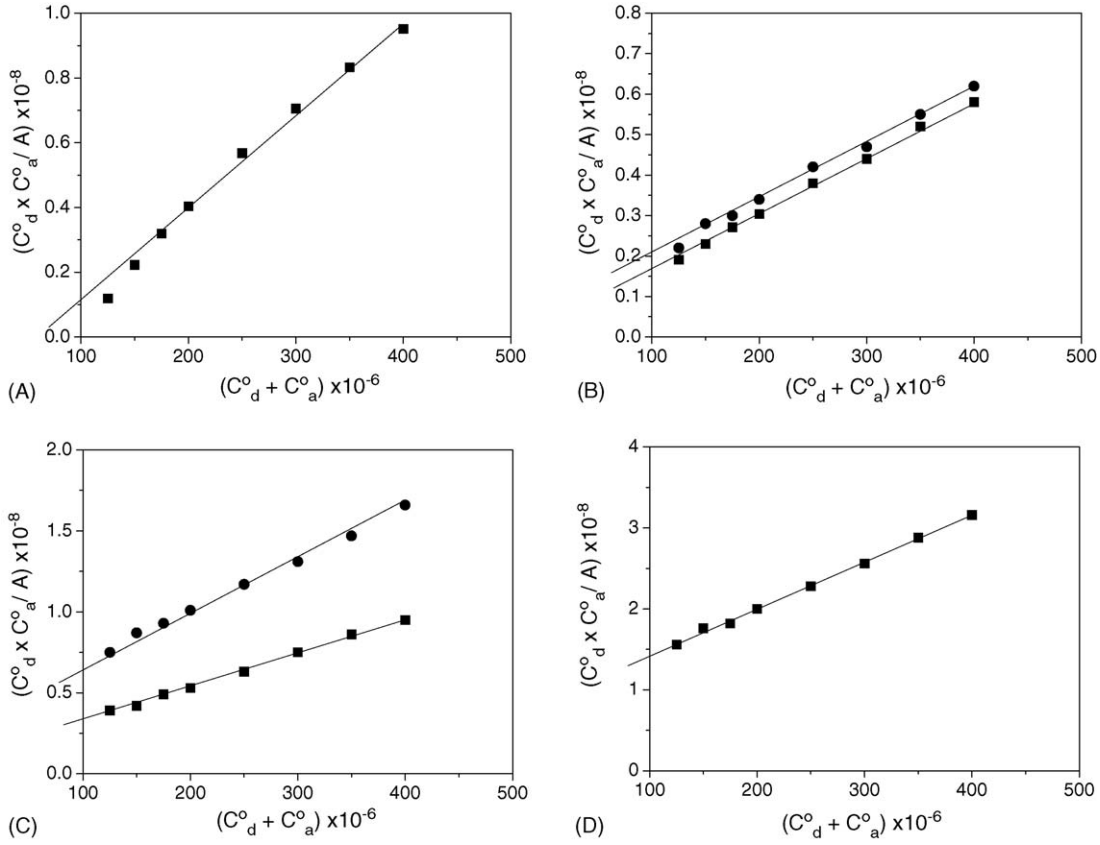


Fig. 3. The plot of $(C_a^0 \times C_d^0)/A$ values against $(C_a^0 + C_d^0)$ values for the donor–acceptor reactions in $CHCl_3$. (A) [(*o*-Tolidine) (DCQ)] reaction at 301 nm; (B) [(*o*-tolidine) (DNB)] reaction at 249 and 291 nm; (C) [(*p*-toluidine) (DCQ)] reaction at 245 and 270 nm; (D) [(*p*-toluidine) (DNB)] reaction at 290 nm.

If we carefully examine the donation sites through HNMR spectra in both *o*-tolidine and *p*-toluidine ($-NH_2$ groups and aromatic rings) and if also carefully examine the acceptors sites in the other side (COOH and NO_2 groups in the DNB sites and chloro group in DCQ), we will come up with some primary results:

(i) There was a decrease in intensity for the peaks that distinguish the $-NH_2$ group (the donation sites for both *o*-tolidine and *p*-toluidine) and also there was shifting for the peaks towards the lower wavenumbers. We can say that the donation process has been carried out by $-NH_2$ group in the case of DCQ and also in the case of DNB.

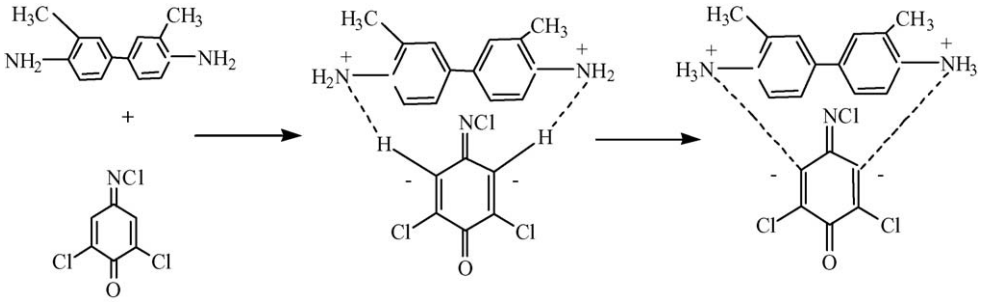
(ii) It was noticed also that the interaction between *o*-tolidine and *p*-toluidine with 3,5-dinitrobenzoic acid does not result in −COOH group character in addition to the above mentioned change (i) in the resulting CT-complexes. This justifies the complexation between $-NH_2$ and −COOH group in 3,5-dinitrobenzoic acid (i.e. intermolecular hydrogen bond formed lead to the absence of the wavenumber of the peak of free carboxylic group of DNB at 1704 cm^{-1} which existed before complexation) indicated in IR spectra.

(iii) In Table 3, there was a shift in the intensity of the aromatic character peaks for both donors and acceptors, resulted from the π–π* CT-complexes which were originally formed via the benzene rings (electron rich group of *o*-tolidine or *p*-toluidine and both DCQ and DNB (electron acceptors)) [2].

To create harmony between the parts of the study, we embodied the HNMR spectra of the complexes, donors and acceptors in Fig. 5. While their peaks assignments and the structures of donors, acceptors and proposed CT-complexation are given in Scheme 1.

A further study on the CT-complexes of π-acceptors (DCQ and DNB) with both *o*-tolidine and *p*-toluidine are discussed (Scheme 1) to their molecular structure and the different types of interaction involved. There are some changes in the chemical shift values of the CT-complexes rather than the free donor and acceptor. The ^{1}HNMR spectrum of the CT-complex formed from the interaction between *o*-tolidine as a donor with π-electron acceptor (DCQ) has shifted in $-NH_2$ group site of donation from δ 4.77 ppm (S, 4H, two $-NH_2$ group) to δ 4.10-4.60 ppm (br S, 6H, $2 \times NH_3$ group of *o*-tolidine). This shift assures that the two amino groups are mainly involved in the formation of the CT-complex.

The mechanism of this reaction take place as follow:



If we examine the acceptor (DCQ), we find out that two withdrawing halo groups and double bond in the *para* and *ortho* position, respectively, are relative to the 3H and 5H. These withdrawing groups give facility to liberate the protons in position 3H and 5H to make intermolecular hydrogen bond with the lone pair of electron on the nitrogen atoms for the two amino groups of *o*-tolidine. The electron density around protons depends on the degree of electro negativity

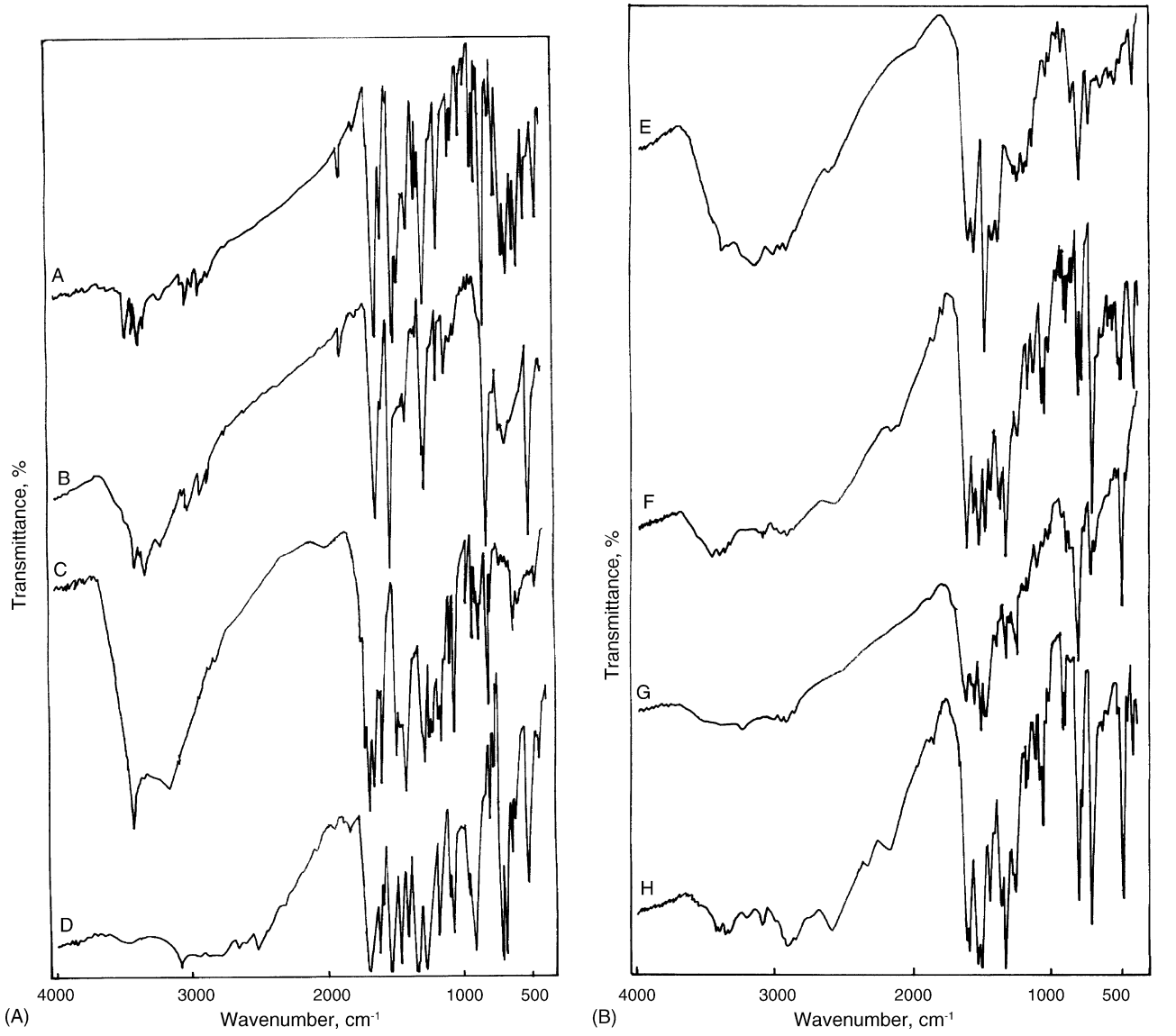


Fig. 4. Infrared spectra of (A) *o*-tolidine; (B) *p*-toluidine; (C) DCQ; (D) DNB; (E) [(*o*-tolidine) (DCQ)]; (F) [(*o*-tolidine) (DNB)]; (G) [(*p*-toluidine) (DCQ)]; (H) [(*p*-toluidine) (DNB)] compounds.

Table 3
Infrared frequencies[a] (cm^{-1}) and tentative assignments[b] for (**1**) *o*-tolidine, (**2**) *p*-toluidine, (**3**) DCQ, (**4**) DNB, (**5**) [(*o*-tolidine) (DCQ)], (**6**) [(*o*-tolidine) (DNB)], (**7**) [(*p*-toluidine) (DCQ)] and (**8**) [(*p*-toluidine) (DNB)]

(**1**)	(**2**)	(**3**)	(**4**)	(**5**)	(**6**)	(**7**)	(**8**)	Assignments
3475 s 3412 s 3375 s 3338 ms	3417 ms 3375 w 3333 ms	3422 s	3460 m, br	3448 w, sh 3380 ms 3344 vw 3323 vw	3543 w,sh 3475 vw 3417 vw 3375 vw 3339 vw	3427 w,br	3433 w 3417 w 3375 w 3359 w 3338 w	ν OH of COOH; DNB ν(NH); NH_2 ν(O—H); water of hydration
3213 ms 3019 s	3223 w 3145 w,sh 3055 vw 3019 ms	3155 s,br 3086 sh 3061sh	3097 mw 2966 vw 2883 vw 2825 vw	3213 sh 3160 vw 3124m,br 3019 w	3113w 3014 vw	3239 mw 3024 vw	3218 w 3108 mw	ν(CH);C═C—H and combination aromatic
2982 ms 2940 mw 2898 w 2856 w	2919 ms 2856 w 2741 vw	–	–	2972 w 2930 w 2862 vw 2804 vw	2977 vw 2935 vw 2877 vw 2783 sh	2966 vw 2930 vw 2872 vw	2998 sh 2925 w 2867 w 2746 vw	ν_{as} CH; —CH_3 + ν_s CH_3
1870 ms	1877 ms 1777 vw	2000 s,br 1735 sh 1700 sh 1670 vs 1640 vs	1971 w 1856 w 1705 vs	2000 ms,sh	1882 w 1814w	1882 w,br 1720 vw 1646 w,sh	2191ms 1908 vw 1882 w	Overtone of: δCH;(out-of-plane) and combination aromatic + ν(C—H); phenyl + ν(C═O) + ν(C═N)
1625 vs 1573 s 1520 w 1489 vs	1625 vs 1594sh 1510 vs	1604 w 1583 vs 1484 s 1447 vw 1405 vs	1631s 1600 ms 1577 vs 1479 vs	1620 s 1578 s 1494 vs 1447 ms 1405 ms	1619 s 1578 ms 1541 s 1494 s 1458 ms 1426 vw	1620 ms 1583 w,sh 1562 ms 1520 s 1489 s 1416 mw	1625 s 1604 s 1541 s 1510s	ν(C═C); aromatic + δ (NH_2) + phenyl nucleus + ν_{as}(NO_2); DNB
1458 s 1384 s 1321 s 1295 s	1447 sh 1405 s 1348 vw 1280 sh	–	1421 vs 1352 vs 1285 vs	1327 vw 1311 vw 1290 w	1384 ms 1348 s	1384sh 1342 s 1311 w 1285 w,sh 1259 s	1458 s 1437 sh 1379 ms 1348 vs 1285 sh	δ_{as} (CH_3) + δ_s (CH_3) ν_s(NO_2); DNB + ν(C—O); COOH
1269 vs 1154 vs 1065 s 1039 s	1269 vs 1222 sh 1180 s 1122 s 1080 w 1049 w	1274 vs 1232 s 1217 s 1164sh 1143 vs 1070 s 1040 vs	1185 vs 1096 ms 1080 vs 1007 vw	1269 mw 1217 mw 1201 w,sh 1154 ms 1133 sh 1065 ms 1033 w	1264 ms 1243 sh 1190 ms 1154 ms 1086 ms 1070 ms 1049 w	1217 vw 1206 vw 1185 w 1122 ms 1080 vw 1044 vw	1264 s 1211 vw 1190 ms 1180 ms 1122 s 1086 w 1065 s 1028 vw	ν(C—O); C—NH_2 + in-plane bending of aromatic CH
986 s 944 ms 902 s 887 s 855 ms 829 vs 777 ms 735 s	986 vw 955 vw 881 sh 813 vs 766 sh 724 vw	949 s 892 sh 860 s 810 sh 798 vs 777 s 719 w 693 w	955 ms 928 vs 866 sh 808 vs 782 ms 729 vs	991 w 876 ms 818 vs 756 s 719 vw	991 vw 949 ms 929 s 913 s 892 vw 876 ms 866 ms 824 s 803 s	944 mw 897 ms 866 sh 818 vs 777 vw	960 vw 928 s 913 s 876 mw 818 vs 719 vs	OH and CH; out-of-plane def. (aromatic ring) + ν(C—N); C—NO_2 + ν(C—Cl); (DCQ)
682 s 661 s 609 s 583 s 525 s 452 s	682 ms, br 635 sh 557 sh 504 vs 473 sh 410 sh	614 s 605 ms 572 w 462 ms 452 ms	646 s 619 ms 536 vs 452 ms	677 w 604 vw 572 w 530 vw 494 vw 447 s	729 vs 688 sh 656 vw 614 ms 583 ms 536 s 525 s 436 s	735 s 708 w 609 vw 577 vw 541 w 509 vs 494 w,sh 473 w	646 w 614w 530 vw 499 vs 467 s 431s	Aromatic ring character of *ortho* subtitution + NH_2 def. + δ_b (CNO); NO_2

[a] s = strong, w = weak, m = medium, sh = shoulder, v = very, br = broad
[b] ν, stretching; δ, bending.

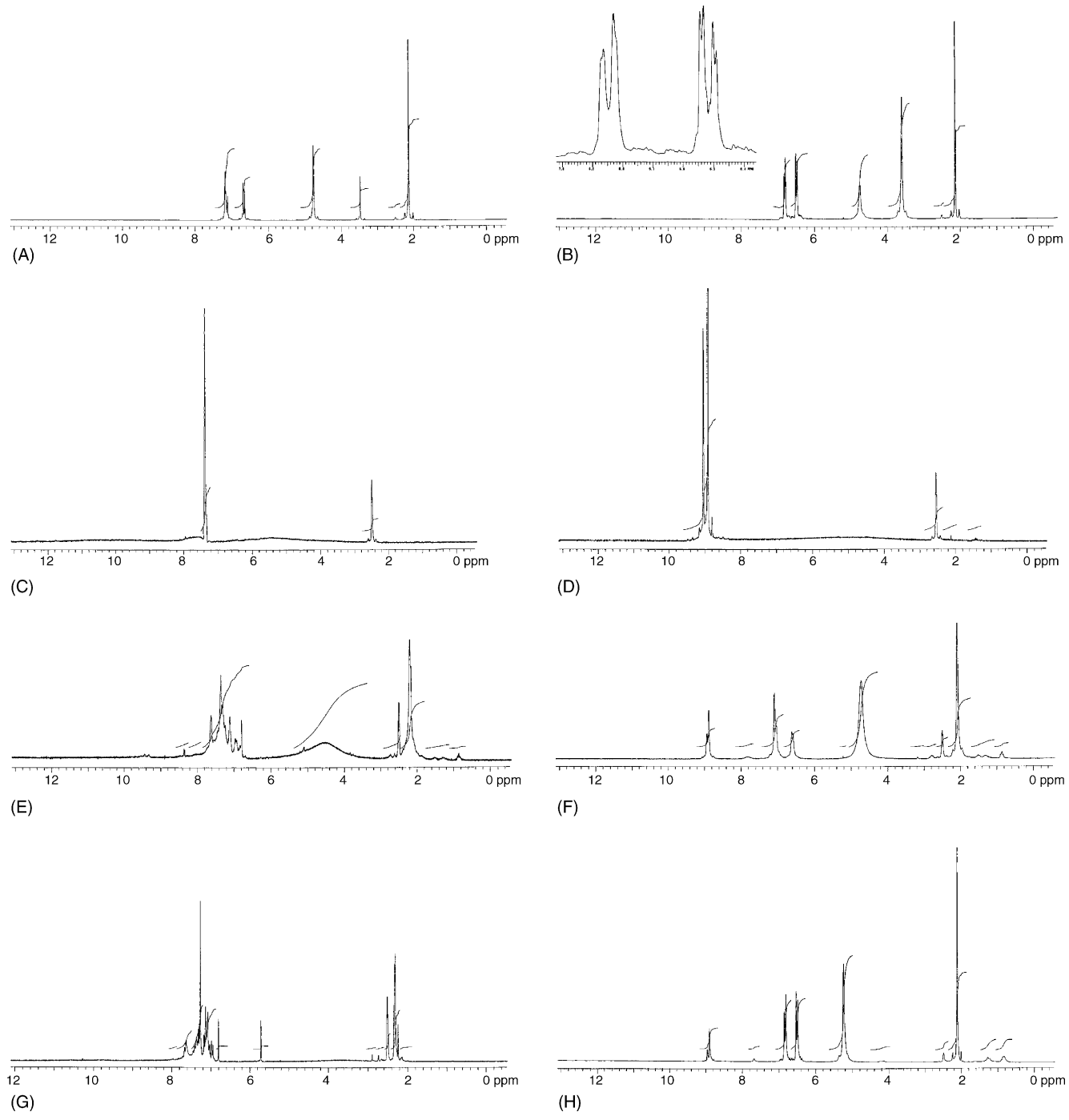
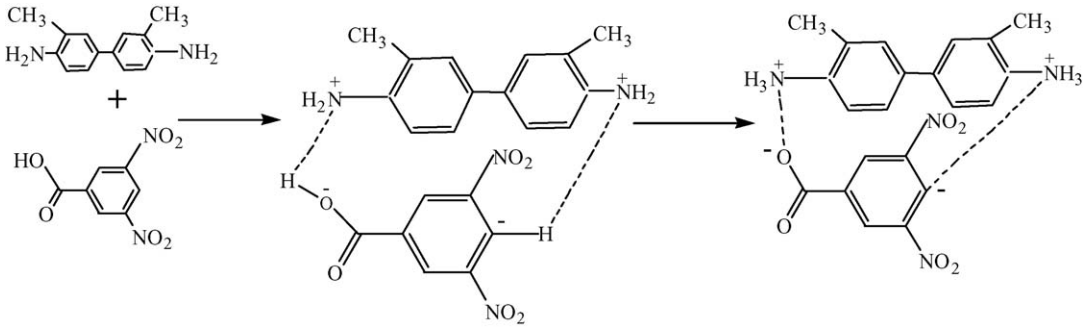


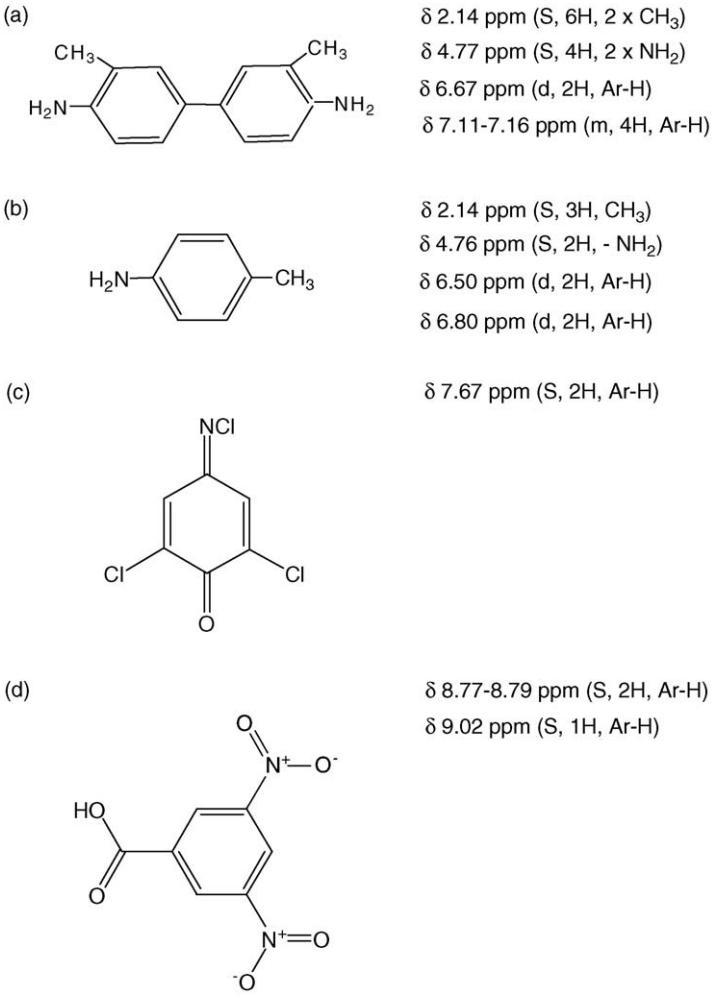
Fig. 5. ^{1}HNMR spectra of (A) *o*-tolidine; (B) *p*-toluidine; (C) DCQ; (D) DNB; (E) [(*o*-tolidine) (DCQ)]; (F) [(*o*-tolidine) (DNB)]; (G) [(*p*-toluidine) (DCQ)]; (H) [(*p*-toluidine) (DNB)] compounds in dmso, δ_{TMS}.

for atoms attached with protons; therefore, the withdrawing groups make decreasing in the electron density around protons and then consecutively increasing in the outer magnetic field intensity which affect the nucleus. Therefore, the chemical transfer for these protons is higher than that of the protons attached to the atom that have a lesser electron negativity. The mentioned above mechanism was supported by the elemental analysis, infrared spectra and the photometric titration which make firm that the ratio occurs by 1:1 (donor:acceptor). The 1:1 molar ratio of (*o*-tolidine: DNB) has been interpreted by using ^{1}HNMR spectrum (Fig. 5, Scheme 1) which concluded in the following mechanism:



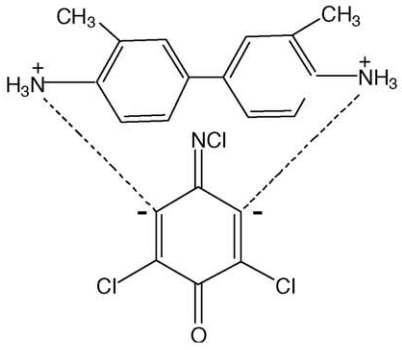
The interaction between *o*-tolidine and DNB occurs through one of the two amino groups in the donor and the H-4 for DNB. The H-4 has more acidic character which facilitates to make intermolecular hydrogen bond with one of amino group because H-4 located in the *ortho* position relative to two nitro groups (withdrawing group), which H-4 became more easy to liberate. The other amino group is attached with proton of the carboxylic group (intermolecular hydrogen bond), this fact was supported beside photometric titration (1:1 ratio) and elemental analysis. In terms of the infrared spectra, the absence of the carboxylic group character and the disappearance of the value of ν(C=O) of the –COOH group around 1700 cm^{-1}, illustrated in the free acceptor (DNB), were clearly indicated.

Concerning, the [(*p*-toluidine) (DCQ)] and [(*p*-toluidine) (DNB)] the chemical shift in the amino group for both these CT-complexes (δ 5.72 ppm and δ 5.25 ppm for [(*p*-toluidine)



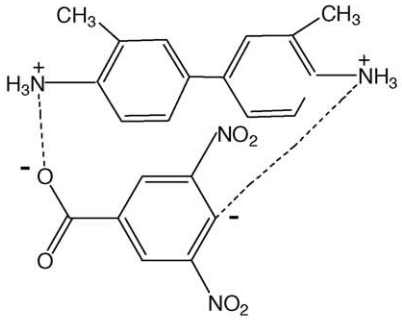
Scheme 1. ^{1}HNMR of (a) *o*-tolidine; (b) *p*-toluidine; (c) DCQ; (d) DNB; (e) [(*o*-tolidine) (DCQ)]; (f) [(*o*-tolidine) (DNB)]; (g) [(*p*-toluidine) (DCQ)]; (h) [(*p*-toluidine) (DNB)] compounds in dmso, δ_{TMS}.

(e)



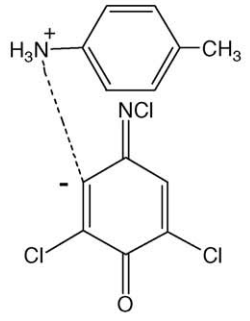
δ 2.16 ppm (S, 6H, 2 x CH_3)
δ 4.10 - 4.60 ppm (br.S, 6H, 2 x NH_3)
δ 6.8-7.43 ppm (m, 6H, Ar-H)

(f)



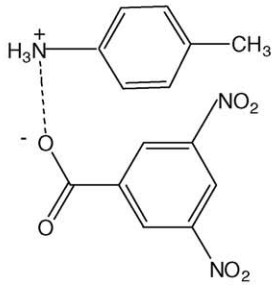
δ 2.09 ppm (S, 6H, 2 x CH_3)
δ 4.40-4.90 ppm (br.S, 6H, 2 x NH_3)
δ 6.62 ppm (d, 2H, Ar-H)
δ 7.05-7.11 ppm (br.S, 4H, Ar-H)
δ 8.90-8.95 ppm (S, 2H, Ar-H)

(g)



δ 2.32 ppm (S, 3H, CH_3)
δ 5.72 ppm (S, 3H, NH_3)
δ 6.80-7.67 ppm (m, 5H, Ar-H)

(h)



δ2.14 ppm (S, 3H, CH_3)
δ 5.25 ppm (S, 3H, NH_3 group)
δ 6.50 ppm (d, 2H, Ar-H)
δ 6.84 ppm (d, 2H, Ar-H)
δ 8.90-8.97 ppm (m, 3H, Ar-H)

Scheme 1. (*Continued*).

(DCQ)] and [(*p*-toluidine) (DNB)] respectively) in the direction of downfield is caused by attachment of *p*-toluidine ring by electron withdrawing groups. The displacement found in the protons of benzene ring of *p*-toluidine to the downfield direction lead us to make sure that this is attached with a nucleus of electron withdrawing group. The chemical shift of protons in DNB and DCQ towards upfield indicates that these acceptors are attached to electron donating groups. The interaction between *p*-toluidine and DCQ occurs through the $-NH_2$ group and the H-3 or H-5 in DCQ in equal amounts. On the other side the CT-complexation of *p*-toluidine with DNB occurs between $-NH_2$ and $-COOH$ groups to form intermolecular hydrogen bond as we discussed in Scheme 1.

Finally, we deduced that both of the *o*-tolidine and *p*-toluidine reacts with various π-acceptors (DCQ and DNB) in $CHCl_3$ at room temperature to form stable CT-complexes with molar ratio (1:1) although we used two different donors one of them has one $-NH_2$ group and the other has two $-NH_2$ groups. These results studied by using elemental analysis, electronic spectra, infrared spectroscopy, and ^{1}HNMR spectra.

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