Monatshefte für Chemie 135, 1395–1407 (2004)
DOI 10.1007/s00706-004-0217-3

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Studies on Charge-Transfer Complexes of 2,3-Dicyano-1,4-naphthoquinone with Some Ring and *N*-Substituted Anilines

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Received April 15, 2004; accepted April 27, 2004

Summary. The charge-transfer complexes (CT-complexes) between 2,3-dicyano-1,4-naphthoquinone (*DCNQ*) and some aromatic anilines, both ring and *N*-substituted, were studied spectrophotometrically in three chlorinated solvents, *viz.* chloroform, dichloromethane, and 1,2-dichloroethane at different temperatures. All the donors are known to form stable 1:1 stoichiometric complexes with *DCNQ* and their stoichiometry was unaffected by the variation of temperature over the studied range. The change in polarity of the solvent also doesn't affect the stoichiometry of the complexes. The determined formation constant values are in the range of 0.49–10.8 $dm^3 mol^{-1}$, the highest is for the *N*-benzylaniline and the lowest is for *o*-chloroaniline. The effect of functional groups on the aniline moiety towards the strength and its electron releasing property has been discussed. The ΔH, ΔS, and ΔG values are all negative, so the studied complexes are reasonably stable and exothermic in nature. The ionization potentials of the donors were determined using the charge-transfer (CT) absorption bands of the complexes. The dissociation energies (W) of the charge-transfer excited state for the CT-complexes were also determined and are found to be constant.

Keywords. 2,3-Dicyano-1,4-naphthoquinone (*DCNQ*); CT-complex; Spectrophotometric method; Thermodynamic parameters; Spectroscopic parameters.

Introduction

Charge-transfer complexes (CT-complexes) are being regarded as important materials due to their ample applications [1–4]. Such complexes have been reported as important reaction intermediates in many chemical reactions [5, 6]. These complexes have been studied in organic conductors and photoconductors [7, 8]. The question of participation of CT-complexes in organic syntheses, and in understanding reaction mechanisms has long been debated since the classical work of

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Benesi and *Hildebrand* [9], who had studied the interaction of iodine with aromatic hydrocarbons.

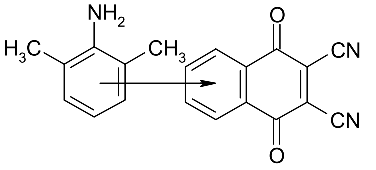
The naphthoquinone derivatives are known to be π-acceptors [10], whose electron accepting ability increases with the introduction of electron withdrawing groups like chloro-, nitro-, cyano- *etc.*, in the naphthoquinone moiety [11]. These groups have large *Hammett* constants and are strongly electronegative [12]. Anilines and its derivatives have considerable donor strength but as donor molecules, they can't be classified into either n-donors or π-donors because the lone pair orbital electrons on the nitrogen atom of the amine group enter in conjugation with the π-orbitals of the benzene ring. The donor properties of the anilines increase when a methyl group is introduced either on the nitrogen atom or in the benzene ring, due to the inductive and hyperconjugative effects of methyl groups.

The present work deals with the study of CT-complex formation between *DCNQ* and different aniline derivatives, *viz.* 2,6-dimethylaniline, *N*-benzylaniline, *m*-chloroaniline, and *o*-chloroaniline. The spectral characteristics of the CT-bands, the equilibrium and thermodynamic parameters of the complexes are investigated. The role of the molecular structure of the donor on the formation of complexes, as well as the effect on donor strength by different types of substitution on the aniline moiety is discussed.

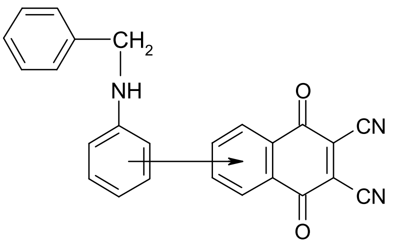
Results and Discussion

The Spectral Characteristics of the CT-Bands

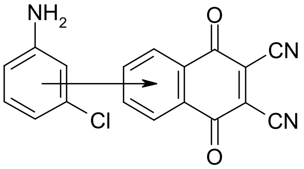
The absorption band in the visible region of the intramolecular CT-complex originates from the electronic transition between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of itself [13]. In contrast, an electron transfer between the molecules is the reason for the absorption in the intermolecular CT-complex. The electronic absorption spectra of the CT-complexes of the mentioned systems were recorded using a constant concentration of the acceptor with varying concentrations of the donor at four different temperatures in the range of 20–50°C. In the present study for every measurement the maintained condition is that concentrations of donor were higher than those of the acceptor, *i.e.* $c_D{}^0 \gg c_A{}^0$, where $c_D{}^0$ and $c_A{}^0$ are the initial molar concentrations of the donor and acceptor molecules respectively. The absorption spectra of mixed donor and acceptor solutions are characterized by the appearance of a new absorption band in the visible region (555–655 nm), neither donor nor acceptor alone absorb in this region. This new absorption band is attributed to the formation of CT-complexes and these complexes are stable under the studied conditions. The representative CT spectra formed between *DCNQ* (10^{-4} *M*) and *N*-benzylaniline in dichloromethane at 20°C are shown in Fig. 1. The wavelength, frequency, and wave numbers corresponding to the absorption maxima of the complexes have been tabulated in Table 1. As can be observed, the absorption maxima of the complexes are mainly dependent on the functional groups and their position on the aromatic ring of aniline. The CT-complexes formed between *DCNQ* and different aromatic anilines may be represented schematically as shown below.



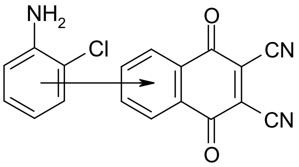
DCNQ-2,6-dimethylaniline complex



DCNQ-*N*-benzylaniline complex



DCNQ-*m*-chloroaniline complex



DCNQ-*o*-chloroaniline complex

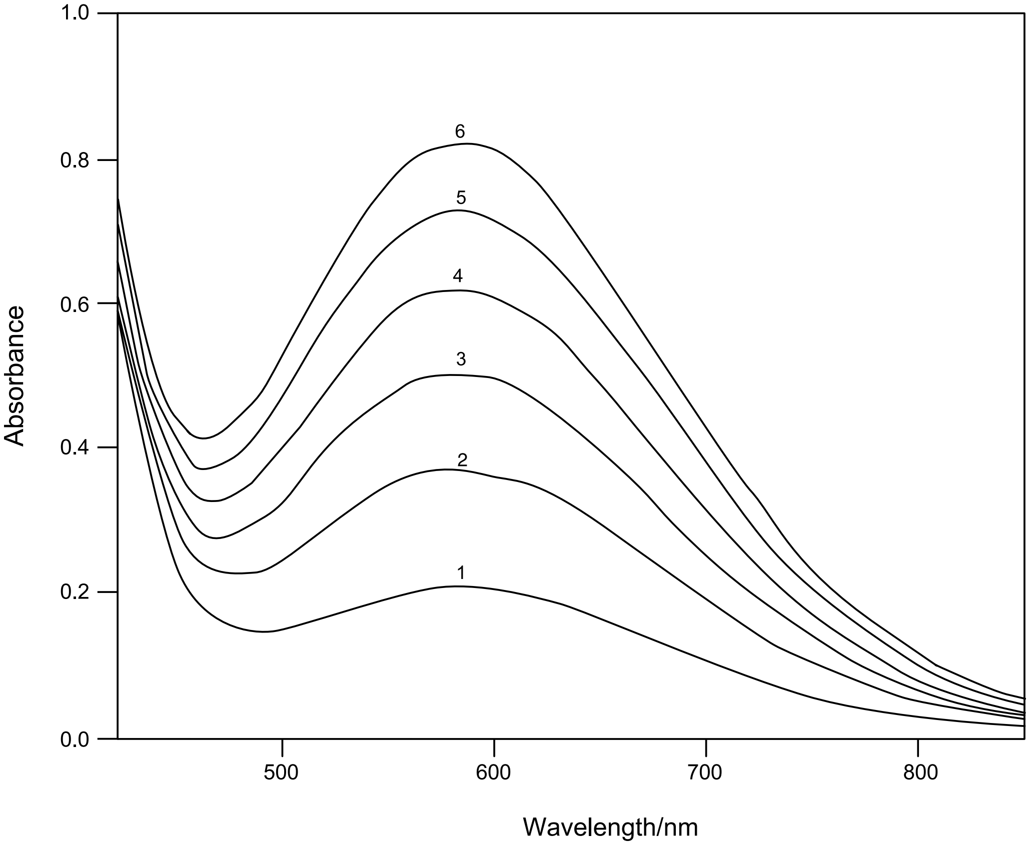


Fig. 1. Absorption spectra of 2,3-dicyano-1,4-naphthoquinone-*N*-benzylaniline complex at various concentrations of the donor in dichloromethane at 20°C

Table 1. The absorption maxima of the charge-transfer complexes of 2,3-dicyano-1,4-naphthoquinone with various aromatic anilines in different solvents at 20°C

Donor	Solvent	λ_{max}/nm	$\nu_{max} \cdot 10^{-14}/\mathrm{sec}^{-1}$	$\bar{\nu}_{max}/\mathrm{cm}^{-1}$
2,6-dimethylaniline	chloroform	660.3	7.9585	15144
	dichloromethane	655.0	7.8946	15847
	1,2-dichloroethane	661.2	7.9694	15124
N-benzylaniline	chloroform	590.0	7.1112	16949
	dichloromethane	585.8	7.0606	17070
	1,2-dichloroethane	587.2	7.0775	17029
m-chloroaniline	chloroform	558.3	6.7291	17911
	dichloromethane	556.6	6.7086	17966
	1,2-dichloroethane	556.7	6.7098	17996
o-chloroaniline	chloroform	575.4	6.9352	17379
	dichloromethane	570.8	6.8798	17519
	1,2-dichloroethane	571.4	6.8870	17500

Formation Constants and Molar Extinction Coefficients of the Charge-Transfer Complexes

Due to the fact that the *Benesi-Hildebrand* method [14] of analysis fails to distinguish the CT-complexes of 1:1 stoichiometry from others, which may also be present in solution, it is more appropriate to use the *Rose-Drago* treatment which, however, distinguishes the species of 1:1 stoichiometry from others [15]. Thus, the

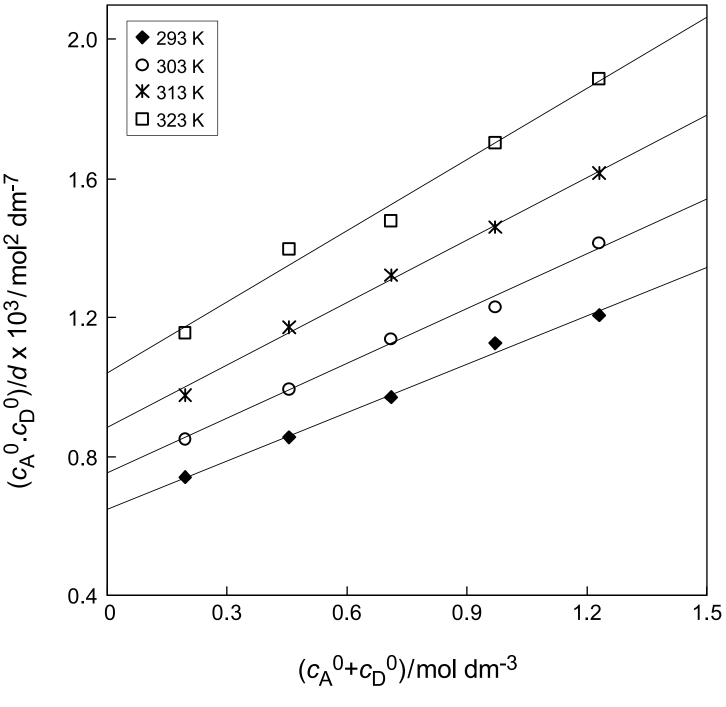


Fig. 2. *Rose-Drago* linear plot for 2,3-dicyano-1,4-naphthoquinone-*m*-chloroaniline complex in 1,2-dichloroethane

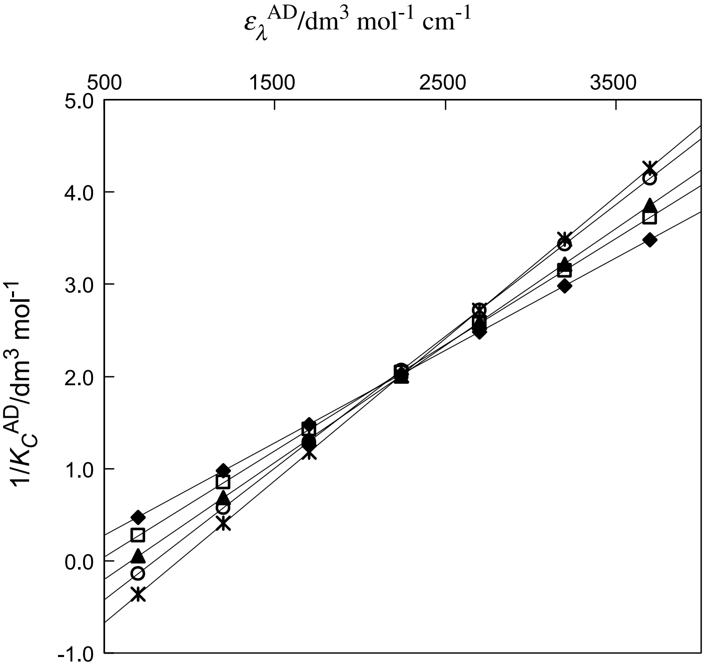


Fig. 3. *Rose-Drago* intersection plot for 2,3-dicyano-1,4-naphthoquinone-*o*-chloroaniline complex in 1,2-dichloroethane at 50°C

Rose-Drago method was used to calculate the formation constant $(K_C{}^{AD})$ and the molar extinction coefficient $(\varepsilon_\lambda{}^{AD})$ of the complexes. For all the systems of *DCNQ* with various aromatic anilines, good linear and intersection plots were acquired from the *Rose-Drago* method, which is applicable due to the existence of 1:1 stoichiometric species. Similar patterns were observed for all the temperatures and solvents, indicating that the stoichiometry of the complexes is 1:1 and is unaffected by the variation of temperature and the change in the dielectric constant of the medium. The representative *Rose-Drago* linear and intersection plots obtained for one of the systems are shown in Figs. 2 and 3, respectively. The values of formation constants and molar extinction coefficients were calculated using such plots and are given in Table 2. As could be observed from the reported $\varepsilon_\lambda{}^{AD}$ values, there is a slight decrease with rising temperature in most cases. The decrease in $\varepsilon_\lambda{}^{AD}$ values with rising temperature is in agreement with *Mulliken's* theory [16] and can be attributed to the broadening of the CT bands with increase in temperature. The observed decrease in formation constant values with rise in temperature indicates the exothermic nature of the interaction between the studied acceptor and donor molecules. The relative order of donor strength, based on the magnitudes of $K_C{}^{AD}$ values, was found to be:

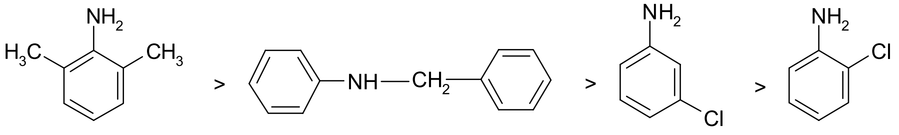


Table 2. The formation constants ($K_C{}^{\mathrm{AD}}$) and molar extinction coefficients ($\varepsilon_\lambda{}^{\mathrm{AD}}$) for CT-complexes formed between 2,3-dicyano-1,4-naphthoquinone and various aromatic anilines in different solvents at different temperatures

Donor	Solvent	$\theta/^\circ\mathrm{C}$	$(K_C{}^{\mathrm{AD}})/\mathrm{dm}^3\,\mathrm{mol}^{-1}$	$(\varepsilon_\lambda{}^{\mathrm{AD}})/\mathrm{dm}^3\,\mathrm{mol}^{-1}\,\mathrm{cm}^{-1}$
2,6-dimethylaniline	chloroform	20	10.80 ± 0.08	3517.68 ± 59
		30	07.91 ± 0.04	3362.14 ± 71
		40	05.83 ± 0.05	3285.42 ± 53
		50	05.79 ± 0.06	2612.33 ± 14
	dichloromethane	20	7.02 ± 0.02	3330.09 ± 11
		25	5.98 ± 0.02	3573.87 ± 87
		30	5.02 ± 0.02	3545.83 ± 87
		35	4.53 ± 0.07	3444.86 ± 14
	1,2-dichloroethane	20	7.20 ± 0.02	3020.71 ± 18
		30	5.71 ± 0.07	2624.53 ± 25
		40	3.77 ± 0.03	2780.17 ± 24
		50	2.29 ± 0.02	3241.85 ± 24
N-benzylaniline	chloroform	20	4.76 ± 0.06	1181.44 ± 20
		30	3.17 ± 0.04	2560.12 ± 29
		40	2.90 ± 0.02	1880.96 ± 32
		50	2.73 ± 0.04	2308.75 ± 24
	dichloromethane	20	4.30 ± 0.06	1818.15 ± 26
		25	3.78 ± 0.02	1742.82 ± 45
		30	3.65 ± 0.03	1606.52 ± 31
		35	2.45 ± 0.01	2224.90 ± 45
	1,2-dichloroethane	20	3.23 ± 0.02	1418.98 ± 55
		30	3.04 ± 0.09	2078.62 ± 96
		40	2.90 ± 0.02	1351.83 ± 33
		50	2.18 ± 0.03	1647.46 ± 26
m-chloroaniline	chloroform	20	1.37 ± 0.001	1869.79 ± 13
		30	1.11 ± 0.001	1855.51 ± 14
		40	1.08 ± 0.001	1595.88 ± 12
		50	1.07 ± 0.002	1404.58 ± 13
	dichloromethane	20	0.90 ± 0.002	1843.46 ± 14
		25	0.80 ± 0.002	1887.93 ± 15
		30	0.68 ± 0.002	1947.91 ± 12
		35	0.58 ± 0.002	2030.88 ± 10
	1,2-dichloroethane	20	0.71 ± 0.002	2157.17 ± 13
		30	0.70 ± 0.002	1897.64 ± 13
		40	0.68 ± 0.001	1664.48 ± 13
		50	0.66 ± 0.002	1460.69 ± 10
o-chloroaniline	chloroform	20	1.24 ± 0.005	2365.16 ± 57
		30	1.00 ± 0.004	2369.38 ± 58
		40	0.90 ± 0.007	2179.99 ± 70
		50	0.81 ± 0.004	1997.13 ± 49

(*continued*)

Table 2 (*continued*)

Donor	Solvent	$\theta/°C$	$(K_C{}^{AD})/\mathrm{dm^3\,mol^{-1}}$	$(\varepsilon_\lambda{}^{AD})/\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$
	dichloromethane	20	0.76 ± 0.003	2548.56 ± 65
		25	0.67 ± 0.003	2553.98 ± 58
		30	0.64 ± 0.003	2479.17 ± 59
		35	0.60 ± 0.003	2447.11 ± 52
	1,2-dichloroethane	20	0.70 ± 0.002	2100.26 ± 49
		30	0.59 ± 0.003	2391.70 ± 63
		40	0.52 ± 0.002	2314.36 ± 52
		50	0.49 ± 0.002	2159.64 ± 53

Of the four donors studied, 2,6-dimethylaniline appears to be the strongest due to the combined effect of two $-CH_3$ groups, which are in ortho-position to the $-NH_2$ group. Methyl groups are well known for their electron repelling effects and hence when they are adjacent to each other, they contribute maximally to the π-electron density of the aromatic ring. In case of *N*-benzylaniline, the very strong electron repelling effect of the $-NH-(CH_2-Ph)$ group makes the *N*-benzylaniline next in the order of the donor strength. Presumably it is stronger than the *m*-chloroaniline because the electron repelling effect of the chloro-group at the meta-position is less compared to the $-CH_3$ groups. *o*-Chloroaniline is weakest of all the donors, due to the steric hindrance of the chloro-group in ortho-position to the $-NH_2$ group its electron releasing ability somewhat decreases. Thus the methyl group substitution either in the ring or on the nitrogen atom of aniline makes a stronger donor.

Thermodynamic Parameters and Spectral Properties of the CT-Complexes

The thermodynamic parameters *viz.*, *Gibb*'s free energy, enthalpy, and entropy changes were evaluated from the computed values of $K_C{}^{AD}$ at different temperatures using the *van't Hoff* plots shown in Fig. 4. The parameters thus obtained are represented in Table 3, the values of free energy changes and entropy shows that complexation is thermodynamically favoured. Even though the enthalpy of the complexation is comparatively low, it is significant to the formation of the complex and its stability. These parameters also reveal that the CT-complex formation between the used donors and the acceptor is of exothermic in nature. A large negative value of these quantities indicates the formation of stronger complexes between the studied donors and the acceptor. *Andrews* and *Keefer* [17] have earlier demonstrated that ΔH and ΔS values generally become more negative as the stability constant for molecular complexes increases. As the binding between donor and acceptor becomes stronger, ΔH would be expected to have higher negative values. The negative values of ΔH are a pointer to the strength of the binding between *DCNQ* and aromatic anilines, and the high stability of the resultant CT-complex.

Additional support for 1:1 stoichiometry of the complexes are the spectroscopic parameters, *viz.* oscillator strength (f), which is a measure of integrated intensity of the CT-band [18–20] and transition moment (μ_{EN}). These parameters

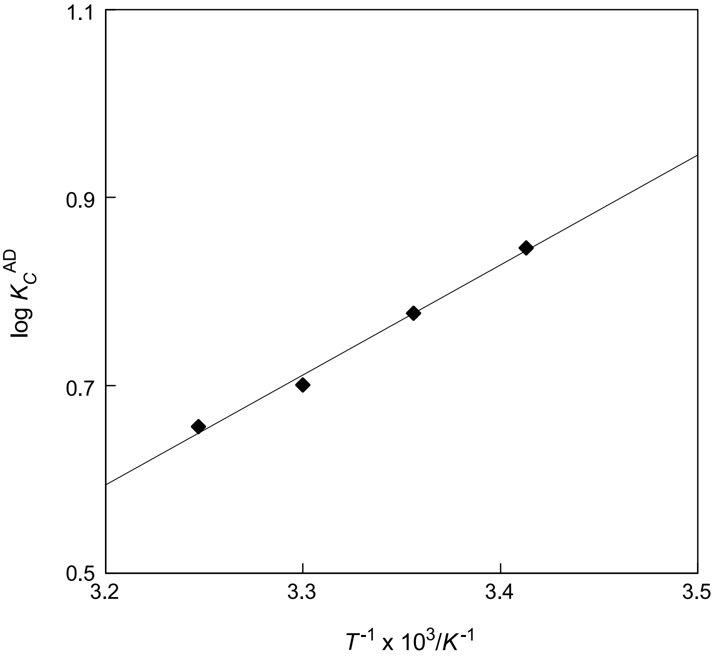


Fig. 4. *van't Hoff* plot for 2,3-dicyano-1,4-naphthoquinone-2,6-dimethylaniline complex in dichloromethane

Table 3. Thermodynamic parameters of the complexes of 2,3-dicyano-1,4-naphthoquinone with various aromatic anilines in different solvents at 293 K

Donor	Solvent	$-\Delta H/\mathrm{kJ\,mol^{-1}}$	$-\Delta S/\mathrm{J\,mol^{-1}\,K^{-1}}$	$-\Delta G/\mathrm{kJ\,mol^{-1}}$
2,6-dimethylaniline	$CHCl_3$	17.26 ± 0.69	39.11 ± 01.17	5.80 ± 0.23
	CH_2Cl_2	22.40 ± 0.67	60.24 ± 01.51	4.75 ± 0.16
	$C_2H_4Cl_2$	31.13 ± 0.78	88.04 ± 03.08	4.89 ± 0.09
N-benzylaniline	$CHCl_3$	13.76 ± 0.48	13.76 ± 0.55	3.78 ± 0.09
	CH_2Cl_2	25.72 ± 1.03	75.65 ± 2.27	3.55 ± 0.11
	$C_2H_4Cl_2$	09.57 ± 0.38	22.91 ± 0.80	2.86 ± 0.07
m-chloroaniline	$CHCl_3$	06.01 ± 0.21	17.90 ± 0.36	0.76 ± 0.02
	CH_2Cl_2	21.73 ± 0.87	75.04 ± 2.25	0.26 ± 0.01
	$C_2H_4Cl_2$	02.06 ± 0.04	09.84 ± 0.34	0.82 ± 0.02
o-chloroaniline	$CHCl_3$	11.12 ± 0.39	36.14 ± 1.08	0.53 ± 0.01
	CH_2Cl_2	11.68 ± 0.47	42.08 ± 0.84	0.65 ± 0.02
	$C_2H_4Cl_2$	13.06 ± 0.33	45.88 ± 1.38	0.38 ± 0.01

have been calculated by using the equations given by *Tsubumora* and *Lang* [21]. The values of f and μ_{EN} thus obtained are tabulated in Table 4, the near constancy of these two parameters is an additional support for the confirmation of 1:1 stoichiometric [22] complex formation between *DCNQ* and the donors studied.

Table 4. Spectroscopic parameters of 2,3-dicyano-1,4-naphthoquinone with various aromatic anilines in different solvents at different temperatures

Donor	Solvent	$\theta/°\mathrm{C}$	$\bar{\nu}_{\mathrm{max}}/\mathrm{cm}^{-1}$	$\Delta\bar{\nu}_{0.5}/\mathrm{cm}^{-1}$	$f/\mathrm{m\,mol}^{-1}$	μ_{EN}/debyes
2,6-dimethylaniline	$CHCl_3$	20	15028.93	45055.31	0.6846	9.8379
		30	15184.80	44089.53	0.6403	9.4654
		40	15158.07	43520.65	0.6176	9.3038
		50	15200.88	41249.05	0.4655	8.0616
	CH_2Cl_2	20	15095.92	46525.27	0.6693	9.7041
		25	15096.83	43618.15	0.6734	9.7342
		30	15150.36	43428.41	0.6652	9.6570
		35	15193.80	42722.60	0.6357	9.4272
	$C_2H_4Cl_2$	20	15001.66	44416.05	0.5796	9.0590
		30	15143.68	42552.79	0.4824	8.2265
		40	15175.24	42987.26	0.5162	8.5014
		50	15174.79	41699.14	0.5839	9.0417
N-benzylaniline	$CHCl_3$	20	16880.77	47846.13	0.2441	5.5432
		30	16829.94	50640.73	0.5600	8.4073
		40	17048.57	45849.28	0.3725	6.8125
		50	17039.26	46483.73	0.4636	7.6020
	CH_2Cl_2	20	17060.47	42482.58	0.3336	6.4451
		25	17035.68	43822.79	0.3299	6.4142
		30	17094.66	43343.59	0.3008	6.1139
		35	17088.98	43388.42	0.4170	7.2001
	$C_2H_4Cl_2$	20	17041.60	41850.00	0.2565	5.6551
		30	16983.73	45023.08	0.4042	7.1109
		40	17016.15	44635.08	0.2606	5.7038
		50	17071.87	43019.69	0.3061	6.1725
m-chloroaniline	$CHCl_3$	20	17756.65	47538.62	0.3895	6.8267
		30	17895.94	46222.02	0.3705	6.6319
		40	17992.20	45721.01	0.3152	6.1001
		50	17999.08	46746.05	0.2836	5.7860
	CH_2Cl_2	20	17929.02	48163.54	0.3835	6.7414
		25	17988.04	47239.62	0.3852	6.7455
		30	17988.06	47239.62	0.3975	6.8518
		35	17986.90	47279.97	0.4148	6.9992
	$C_2H_4Cl_2$	20	17870.76	47709.06	0.4445	7.2699
		30	17934.79	46711.45	0.3829	6.7349
		40	18021.42	45933.85	0.3302	6.2396
		50	18014.21	46880.62	0.2958	5.9062
o-chloroaniline	$CHCl_3$	20	17230.12	47267.84	0.4829	7.7165
		30	17401.67	45233.45	0.4629	7.5180
		40	17345.16	47045.48	0.4430	7.3646
		50	17544.84	44976.59	0.3880	6.8546
	CH_2Cl_2	20	17452.98	45736.31	0.5035	7.8285
		25	17514.03	45380.17	0.5006	7.7931

(*continued*)

Table 4 (*continued*)

Donor	Solvent	$\theta/°\mathrm{C}$	$\bar{\nu}_{\max}/\mathrm{cm}^{-1}$	$\Delta\bar{\nu}_{0.5}/\mathrm{cm}^{-1}$	$f/\mathrm{m\,mol}^{-1}$	μ_{EN}/debyes
		30	17532.72	45384.51	0.4860	7.6742
		35	17569.21	45544.94	0.4814	7.6301
	$C_2H_4Cl_2$	20	17418.81	45785.18	0.4154	7.1169
		30	17391.39	46096.96	0.4762	7.6273
		40	17588.96	44671.12	0.4466	7.3439
		50	17599.84	45239.05	0.4220	7.1375

Ionization Potentials of the Donors

Out of the many applications of CT-complexes one important application is to calculate the ionization potentials of the donors. *Briegleb* and *Czekalla* [23] have described a method of determining the ionization potentials of the electron donors from ν_{CT} of the complexes. It may be difficult to determine ionization potentials by other methods such as *Rydberg* series, photoionization, and electron impact, because of the low vapour pressure of some of these substances. Based on the theoretical relationship, *Parrel et al.* [24] suggested an empirical relation between ionization potential and $h\nu_{\mathrm{CT}}$. Thus the ionization potentials of the donors which form complexes with *DCNQ*, were calculated using Eq. (1) where I^{D} is the ionization potential of the donor molecule.

$$h\nu_{\mathrm{CT}}/\mathrm{eV} = 0.82(I^{\mathrm{D}}/\mathrm{eV}) - 4.28 \tag{1}$$

The values of ionization potentials thus determined are given in Table 5. Further evidence for the nature of CT-interaction in the present systems is the calculation of the dissociation energy (*W*) of the charge-transfer excited state of the complexes. Hence the dissociation energies of the complexes were calculated from their CT-energy of the lowest intermolecular CT-band, $h\nu_{\mathrm{CT}}$, the ionization potentials of the

Table 5. Ionization potentials (I^{D}) of donors, dissociation energies (*W*) of the charge-transfer excited states, and CT energy ($h\nu_{\mathrm{CT}}$) of the complexes between 2,3-dicyano-1,4-naphthoquinone with various aromatic anilines in different solvents

Donor	Solvent	I^{D}/eV	$(h\nu_{\mathrm{CT}})$/eV	W/eV
2,6-dimethylaniline	chloroform	7.51	1.88	4.2225
	dichloromethane	7.62	1.97	4.2417
	1,2-dichloroethane	7.51	1.88	4.2220
o-chloroaniline	chloroform	7.85	2.16	4.2834
	dichloromethane	7.87	2.18	4.2872
	1,2-dichloroethane	7.87	2.17	4.2867
m-chloroaniline	chloroform	7.93	2.22	4.2979
	dichloromethane	7.94	2.23	4.2994
	1,2-dichloroethane	7.94	2.23	4.2993
N-benzylaniline	chloroform	7.79	2.10	4.2717
	dichloromethane	7.80	2.12	4.2750
	1,2-dichloroethane	7.80	2.11	4.2739

donors, and electron affinity, E^{A}, of the acceptor using the empirical relation [25] given in Eq. (2).

$$h\nu_{CT} = I^{D} - E^{A} - W \tag{2}$$

The plots of $h\nu_{CT}$ *vs.* I^{D} and W *vs.* I^{D} shown in Figs. 5 and 6 are linear, as was expected. The calculated values of W are included in Table 5. The thus acquired

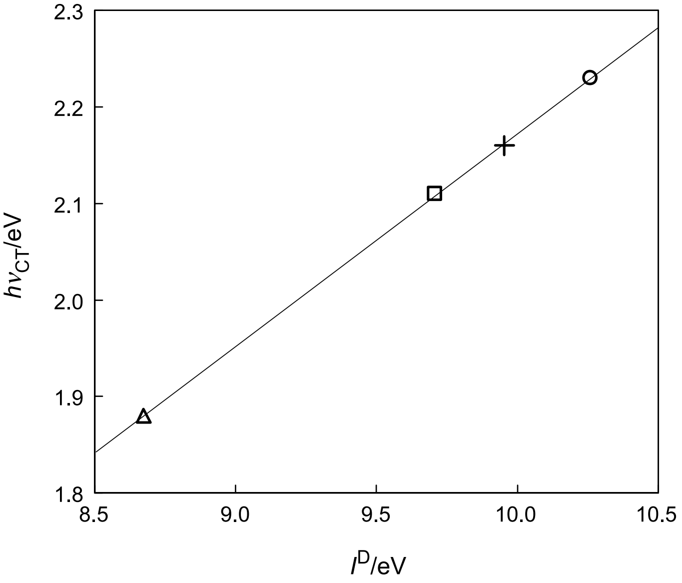


Fig. 5. The plot of $h\nu_{CT}$ *vs.* I^{D} of a series of donors for 2,3-dicyano-1,4-naphthoquinone in chloroform (△: 2,6-dimethylaniline, □: *N*-benzylaniline, +: *o*-chloroaniline, ○: *m*-chloroaniline)

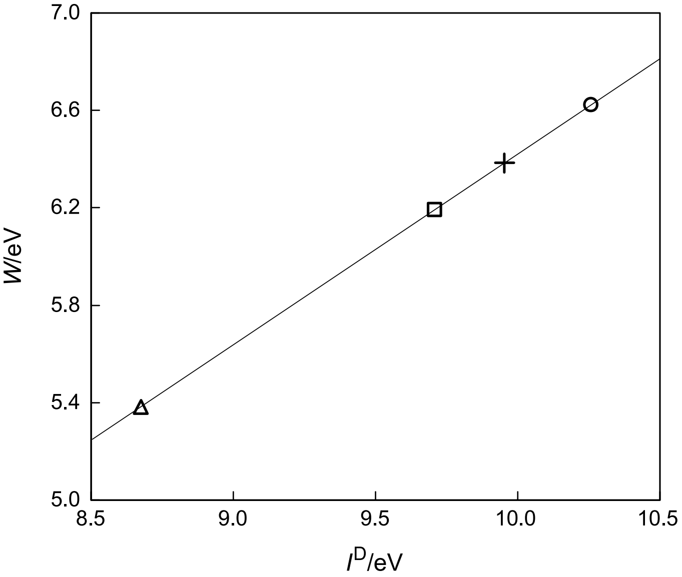


Fig. 6. The plot of W *vs.* I^{D} of a series of donors for 2,3-dicyano-1,4-naphthoquinone in chloroform (△: 2,6-dimethylaniline, □: N-benzylaniline, +: *o*-chloroaniline, ○: *m*-chloroaniline)

values of dissociation energy of charge-transfer excited states of the complexes are constant, which suggests that the investigated complexes are reasonably strong and stable under the studied conditions with higher resonance stabilization energy.

Conclusions

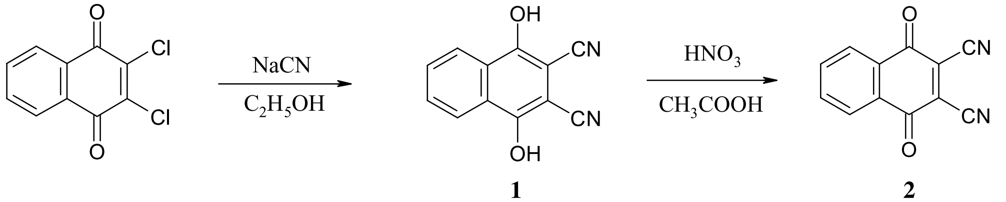
From the foregoing discussions, it may be concluded that the *DCNQ* acceptor forms strong CT-complexes of 1:1 stoichiometry with a set of aromatic anilines in chloroform, dichloromethane, and 1,2-dichloroethane. The stoichiometry of the complexes is unaltered by variation of temperature. The formation constant ($K_C{}^{AD}$), molar extinction coefficient ($\varepsilon_\lambda{}^{AD}$), thermodynamic and spectroscopic parameters of the complexes were found to be highly solvent dependent. The investigated complexes are stable and exothermic in nature.

Experimental

Among the donors used in the present study, *o*- and *m*-chloroanilines were BDH samples while 2,6-dimethylaniline was a Fluka sample and *N*-benzylaniline was an Aldrich sample. The 2,3-dichloro-1,4-naphthoquinone, used as starting material for the synthesis of 2,3-dicyano-1,4-naphthoquinone was from Fluka AG. All the donors were dried over caustic potash (BDH analar) and distilled twice under reduced pressure just before use. The solvents, chloroform (s.d. fine), dichloromethane (Ranbaxy), and 1,2-dichloroethane (s.d. fine) were of spectral grade quality and were used without further purification. In all the spectral measurements, it was verified that solvents did not possess any significant absorption at the wavelength of the measurement.

Preparation of 2,3-Dicyano-1,4-naphthoquinone (DCNQ)

The acceptor used in the present study, 2,3-dicyano-1,4-naphthoquinone (*DCNQ*), was synthesized by the modified method of *Renolds et al.* [26]. It was prepared in two stages, preparation of 2,3-dicyano-1,4-naphthohydroquinone (**1**) followed by its oxidation to 2,3-dicyano-1,4-naphthoquinone (*DCNQ*) (**2**).



1 **2**

2,3-Dicyano-1,4-naphthohydroquinone (**1**)

Four and half grams of 2,3-dichloro-1,4-naphthoquinone were taken in 75 ml of ethanol to which a solution of 6.0 g of sodium cyanide was added slowly with constant stirring. During the addition, the temperature of the reaction mixture was kept below 40°C. After complete addition of the cyanide solution, the reaction mixture was stirred at room temperature for about an hour. The dark red solution was then acidified with ice-cold hydrochloric acid, after filtering the reaction mixture to remove any unreacted 2,3-dichloro-1,4-naphthoquinone. The resulting solid was filtered off, washed with cold water, and dried. The mp of **1** thus obtained was found to be above 300°C.

2,3-Dicyano-1,4-naphthoquinone (DCNQ) (**2**)

A suspension of 5.0 g of **1** in 100 ml of acetic acid was heated on a steam bath and stirred, 15 ml of 30% nitric acid were then added to this mixture in small portions over a period of one hour. Then the clear solution was diluted with water and chilled, thus producing a yellow solid. It was filtered off and dried. The compound was recrystallized twice from dichloromethane and mp of the compound was found to be 267°C. The values of C, H, and N obtained from a Thermo Quest elemental analyzer agreed very well with the expected values. Further, the identity of the synthesized compound was confirmed by FT-IR (Nicolet Impact 410) and NMR (Brucker, 300 MHz) techniques.

The electronic absorption spectra of the complexes were recorded on a Carry-50, double beam Bio UV-VIS spectrophotometer using a matched pair of quartz cells with 10 mm path length having teflon airtight stoppers. The peltier accessory was used to maintain the temperature at the desired value. All measurements were performed using freshly prepared solutions and as far as possible, the solutions were protected from direct sunlight.

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