# Charge-Transfer Complexes of Tertiary Aromatic Amines with Tetracyanoethylene

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Received 14 September 1993
Accepted for publication 28 November 1994

The tertiary aromatic amines *N,N*-diethylaniline, *N*-methyl-*N,N*-diphenylamine, and triphenylamine form charge-transfer complexes with tetracyanoethylene in solutions, which may subsequently undergo further chemical reactions. Using UV VIS and EPR spectroscopies it has been found that for the stability of the complex the delocalization of nonbonding nitrogen electrons, *i.e.* the electron density in the *para* position on the benzene rings of studied amines is important. On the other hand, the values of the ionization potentials are important mainly for the formation of charge-transfer complexes.

It is well known that the charge-transfer (CT) complexes play an important role in the biological systems [1] and in some chemical reactions [2]. The formation of complexes may be expressed by Scheme 1 [3].

$$\mathrm{D + A} \longrightarrow \mathrm{DA} \xrightarrow{\text{solvent}} \mathrm{D^{+\bullet} + A^{-\bullet}} \longrightarrow$$
$$\longrightarrow \text{next reaction products}$$

*Scheme 1*

In this scheme D and A are donor and acceptor molecules, respectively, DA is their CT complex and $D^{+\bullet}$ and $A^{-\bullet}$ are their ion-radicals.

Compounds which have sufficiently low ionization potentials (*e.g.* tertiary amines) [2, 3] can be used as donors of electrons. On the other hand, compounds with high electron affinity, *e.g.* chloranil, nitrobenzenes, iodine, tetracyanoquinodimethane, tetracyanoethylene (*I*), *etc.* can serve as acceptors of electrons.

The tertiary aromatic amines form with *I* rather easily relatively stable CT complexes in a nonpolar solvent. The characteristic feature of these complexes is the appearance of new absorption bands in their absorption spectra. Many of these CT complexes are only intermediates for subsequent chemical reactions [2].

The aim of this paper is the study of the formation of CT complexes and their reaction products among *I* and tertiary aromatic amines; *N,N*-diethylaniline (*II* ), *N*-methyl-*N,N*-diphenylamine (*III*), and triphenylamine (*IV*).

## EXPERIMENTAL

The compound *I* (Lachema, Brno) has been recrystallized from 1,2-dichloroethane and sublimed at 50 °C and 0.1 Pa. Diethylaniline (Lachema, Brno) has been distilled at 1000 Pa. Triphenylamine (Lachema, Brno) has been crystallized from ethyl acetate and sublimed at 100 °C and 0.02 Pa. The compound *III* has been prepared by alkylation of *N,N*-diphenylamine with dimethyl sulfate [4]. All solvents were purified and dried according to [5].

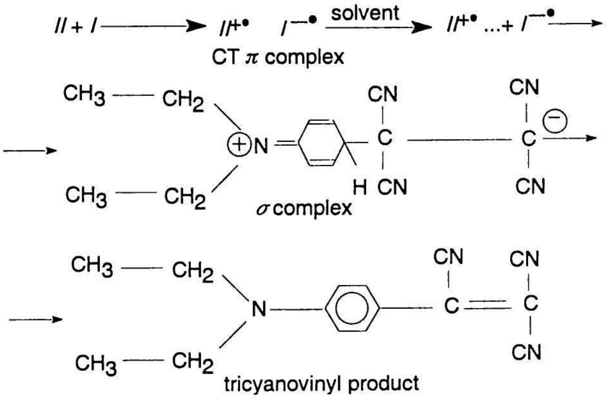
The CT complexes were prepared by the mixing of donor and tetracyanoethylene solutions in the mole ratio 1 1 ($c = 0.05\ \mathrm{mol\ dm^{-3}}$).

The electron spectra were recorded by Specord UV VIS spectrophotometer (Zeiss, Jena). The samples were measured and preserved during the course of the reaction in closed quartz cuvettes ($d = 1$ cm).

The electron paramagnetic resonance (EPR) spectra were recorded by an apparatus ER-9 (Zeiss, Jena) working in the X band.

## RESULTS AND DISCUSSION

In acetonitrile *II* reacts with *I* forming a CT complex ($\lambda = 820$ nm) which changes to the $\sigma$ complex and then in the third step this transforms into 4-tricyanovinyl-*N,N*-diethylaniline ($\lambda = 530$ nm) [6—8]. The course of the reaction between *II* and *I* is illustrated in Scheme 2.



*Scheme 2*

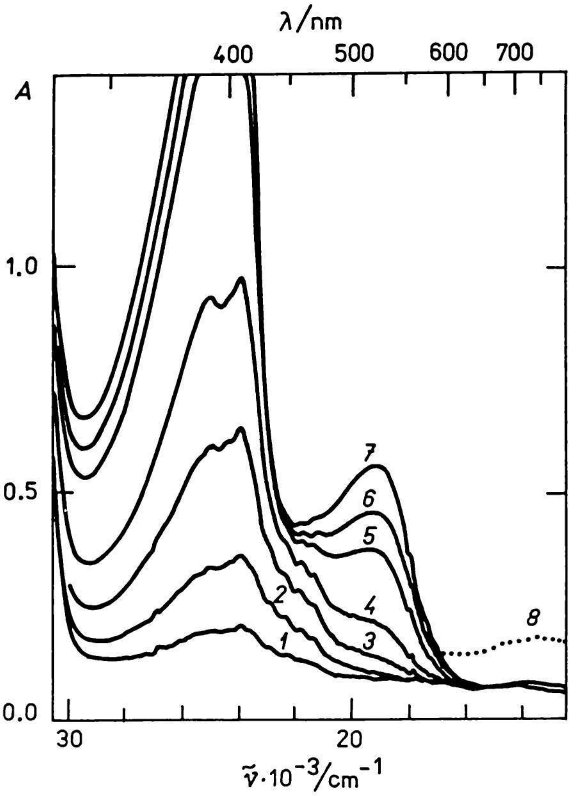


**Fig. 1.** Absorption spectra of the system containing equimolar solutions ($c$ = 0.05 mol dm$^{-3}$) of *II* and *I* in acetonitrile recorded in different time periods after mixing (*1.* 3 min, *2.* 5 min, *3.* 10 min, *4.* 20 min, *5.* 35 min, *6.* 45 min, *7.* 60 min, *8.* immediately after mixing).

The electron transfer from *II* to *I* results in the formation of the ion-radicals which can be observed in polar solvents [9] by means of their absorption spectra (the shoulder with a fine structure at λ = 440 nm on the band at λ = 415 nm in Fig. 1 belongs to $I^{-\bullet}$ [6,10—19]) and using EPR spectroscopy. In Fig. 2 EPR spectrum of the mixture of *II* and *I* in acetonitrile is presented. This spectrum contains nine lines of the hyperfine structure. The intensity ratio of these lines 1 : 4 : 10 : 16 19 16 10 : 4 1 is a result of the hyperfine interaction of an unpaired electron with the four equivalent nitrogen nuclei of *I*. The *g* value of the central line is 2.0046 ± 0.0002, which corresponds to the literature data on $I^{-\bullet}$ [11].

The compound *III* reacts with *I* similarly as *II* but the course of this reaction is slower. In the first step *III* forms with *I* the CT complex in acetonitrile, which is accompanied by the appearance of new absorption bands at λ = 760 nm and 380 nm (Fig. 3, curve *1*). One part of this complex dissociates to ion-radicals according to Scheme 1, which was demonstrated by the appearance of the absorption band at λ = 430 nm (as a shoulder on the peak at λ = 380 nm) which belongs to $I^{-\bullet}$ The other part of the CT complex disappears later and simultaneously we can observe the band characteristic of the final product 4-tricyanovinyl-*N*-methyl-*N*,*N*-diphenylamine. This course of the reaction is documented in the absorption spectrum of this mixture, where the band at λ = 760 nm decreases and the new band at λ = 530 nm appears (Fig. 3, curve *2*). The presence of ion-radicals was supported by EPR spectroscopy, in the EPR spectra of the mixture of *III* and *I* in acetonitrile an unresolved signal at *g* = 2.004 ± 0.0006 was observed. We assume that the

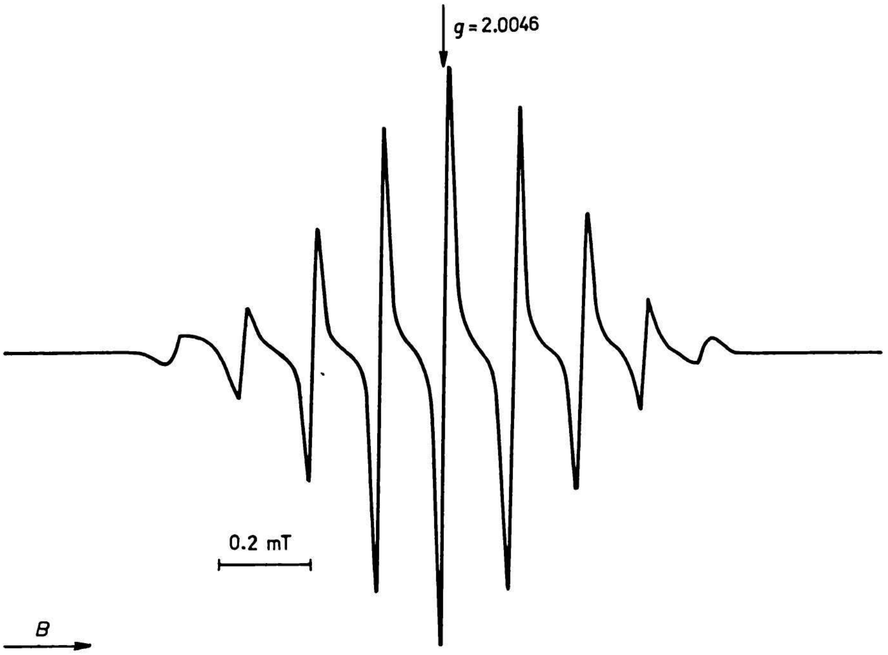


**Fig. 2.** The EPR spectrum of the system containing equimolar solutions ($c$ = 0.05 mol dm$^{-3}$) of *II* and *I* in acetonitrile recorded 15 min after mixing.

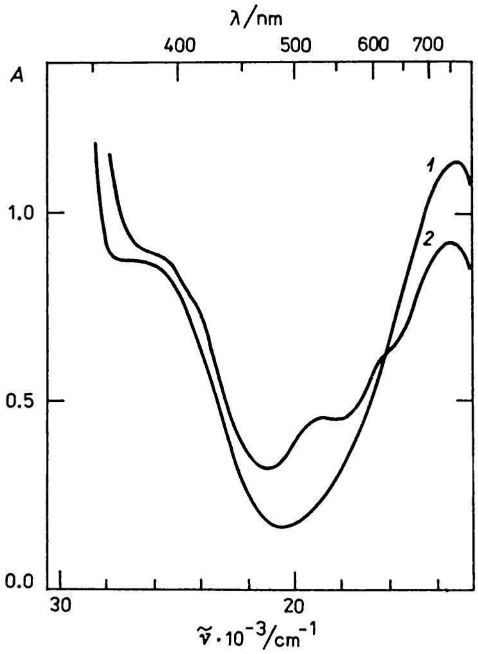


**Fig. 3.** Absorption spectra of the system containing equimolar solutions ($c$ = 0.05 mol dm$^{-3}$) of *III* and *I* in acetonitrile recorded immediately (*1*) and 24 h (*2*) after mixing.

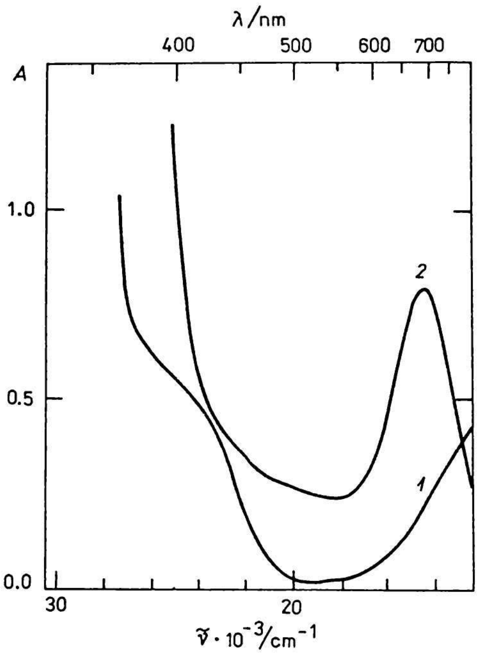
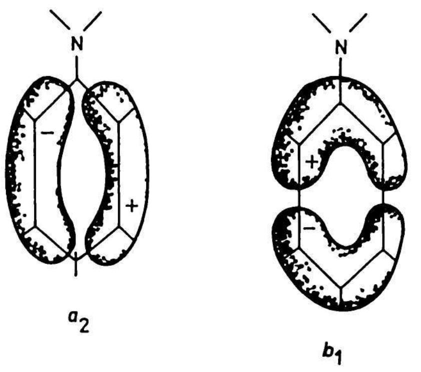


**Fig. 4.** Absorption spectra of the system containing equimolar solutions ($c$ = 0.05 mol dm$^{-3}$) of *IV* and *I* in chloroform recorded 1 h (*1*) and 2 d (*2*) after mixing.

position of this EPR signal corresponds to $I^{-\bullet}$ because its $g$ value is 2.0046 [11].

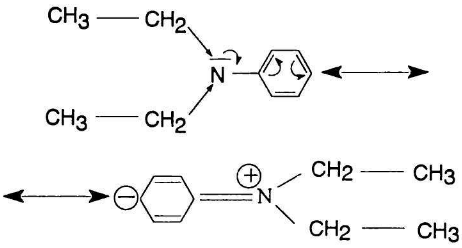
The interaction between *IV* and *I* in chloroform begins with the formation of CT complex, which has absorption bands at $\lambda > 800$ nm and $\lambda \approx 400$ nm (Fig. 4, curve *1*). The CT complex slowly dissociates to $I^{-\bullet}$ and $IV^{+\bullet}$. Two cation radicals of *IV* form the dimer of *N,N,N,N*-tetraphenylbenzidine (*V*) which subsequently interacts with *I* forming a new CT complex again [20]. The new state is manifested in the absorption spectrum of this complex by new absorption bands at $\lambda$ = = 690 nm and 380 nm corresponding to an undissociated complex between *I* and *V* (Fig. 4, curve *2*). This new complex subsequently dissociates to ion-radicals which were detected by the EPR spectroscopy. The EPR spectra of this mixture exhibited an unresolved signal with $g$ = 2.0029 corresponding to $V^{+\bullet}$ [20, 21].



*Scheme 3*

In all studied systems the formed CT complexes are characterized by two CT absorption bands corresponding to electron transitions from $a_2$ and $b_1$ of the highest occupied molecular orbitals of the benzene rings (Scheme 3) [22].

From the obtained results it follows that for the tricyanovinyl reaction the $b_1$ orbital is important as well as a higher electron density in the *para* position to the amino group. For the course of tricyanovinylation the structure of the donor molecules plays an important role. The rate of the tricyanovinylation is the highest for *II* (the tricyanovinyl band was observed immediately after the mixing of the components), which is the result of the high electron density in the *para* position of the benzene ring as it follows from the resonance structures of *II* (Scheme 4).



*Scheme 4*

The presence of the second benzene ring in *III* significantly decreases the rate of tricyanovinylation due to the delocalization of $n$-electrons from nitrogen on two benzene rings (the tricyanovinyl band was observed after several hours).

The decrease of electron density in the *para* position of benzene rings (against *II* and *III*) is the lowest in *IV*. Therefore the tricyanovinyl band was not observed even after several days.

The ionization potentials $I_D$ calculated from the position of CT bands according to the Voigt — Reid equation [23] (Table 1) correspond to the literature data [22]

$$I_D/\mathrm{eV} = \left( \frac{1024}{\lambda_{\max}/\mathrm{nm}} + 4.42 \right) / 0.83$$

**Table 1.** Ionization Potentials of the Studied Tertiary Aromatic Amines Calculated from the Positions of CT Bands

| Compounds | $I_{D2}$/eV | $I_{D1}$/eV |
|---|---|---|
| *II* | — | < 7.14 |
| *III* | 9.14 | 7.23 |
| *IV* | 9.95 | < 7.14 |
| *V* | 9.14 | 7.42 |

It is interesting that the ionization energies (Table 1) do not correspond with the reactivity of amine molecules in tricyanovinyl reactions. However, the delocalization of nonbonding electrons is important for the reactivity of amines and for stability of their CT complexes with *I*, too. The ionization potentials are important mainly for the formation of CT complexes.

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Translated by F. Šeršeň