

Electron transfer and the structural changes in the excited state

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Abstract. Electronic excitation followed or accompanied by electron transfer (ET) between donor (D) and acceptor (A) subsystems leads in the charge-transfer (CT) state to a relaxed molecular structure, often markedly different from the initial one. Special attention is paid to the Twisted Intramolecular Charge Transfer (TICT) excited states. Main factors determining the molecular structure (Coulombic attraction, orbital overlap between D and A, mixing of states, steric effects) are discussed for several typical cases of organic inter-molecular and intra-molecular exciplexes.

INTRODUCTION

Radiative excitation of molecules or molecular systems composed of a donor (D) and acceptor (A) subsystems, variously bridged or forming a weak or encounter complex, often leads to an electron transfer (ET), provided some thermodynamic and kinetic conditions are fulfilled. The ET can be inherently involved in the excitation process (*radiative ET*) if the absorption occurs within a charge transfer (CT) band; or it follows the excitation (excited state reaction of ET). The product can be formed in its ground or excited state. The former process represents an *ET quenching*, the latter leads to an excited CT state; only the last case will be considered below.

Numerous cases can be distinguished. Leaving aside, e.g., the coordination compounds, we shall discuss only some categories frequently met among the organic donor-acceptor systems (Fig.1).

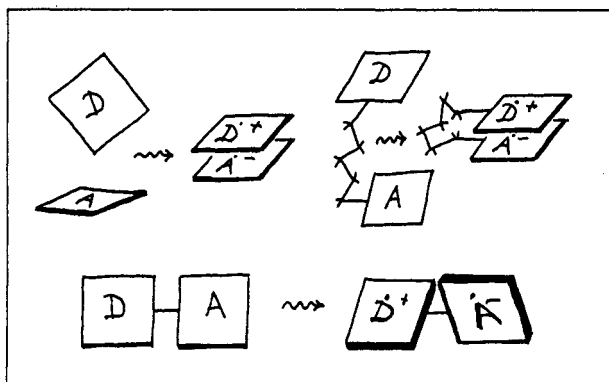


Figure 1. Symbolic representation of the structural changes in the CT states. Top left: inter-molecular exciplex; top right: intra-molecular flexibly bridged exciplex; bottom: twisted intramolecular CT state (TICT).

In the study of molecular structures in the excited states sometimes the theory, sometimes the experiment, get ahead. Often the experimental findings were unexpected. The aim of this paper is to systematize the results, to seek the patterns of similarity, and the origin of differences in the mentioned structural groups of compounds.

MAIN FORCES AND INTERACTIONS

Pure (zero order) CT configurations correspond to molecular geometries with zero overlap between the orbitals of D and A. A prominent factor in the case of *charge separation* is the *Coulombic attraction* of D^+ and A^- , the oppositely charged sub-systems of the product. The ET may occur over a considerable distance, e.g., of 7-8 Å (through space or solvent) or even more (through bonds, *vide infra*). Then, the Coulombic force acting between the opposite charges (in nonpolar or weakly polar solutions) causes what is picturesquely named the *harpooning effect* [1]. This leads to mutual approach, to deformations, and usually to increasing overlap between these moieties.

The last effect results in mixing of other zero order states in the excited CT state. The admixture of higher lying excited states leads to stabilisation of the CT state. Mutual contamination of the CT and the ground state - leads to their repelling, i.e., to the stabilisation of the ground, and destabilisation of the excited CT state. This opposing tendency is one of the important factors, which cause the molecular structure in the excited CT state to differ from that in the ground state.

Some other important factors are to be mentioned.

(i) The solvent polarity effect; with increasing polarity of the medium the CT state with a very large zero order (inherent) dipole moment:

$$\mu_{CT} = \langle \Psi_{CT} | \hat{\mu} | \Psi_{CT} \rangle \quad (1)$$

is strongly stabilized. Along with this stabilisation, due to the energy difference factors, the excited CT state becomes less contaminated with the higher lying less polar states, whereas the mutual mixing of the ground and excited state may somewhat increase, which depends on the energy gap and symmetry.

The analyses of molecular structures in the excited CT states along these lines, including the solvent polarity effect, have been done by numerous authors, to mention specially the already classical paper by Beens and Weller [2].

(ii) The repulsive nonbonding interactions (steric effects) affect often in a decisive way both the reaction (relaxation) path, and the final structure of the excited CT state. This will be demonstrated specially on the case of the TICT states.

(iii) In most cases the molecular geometries of the parent molecular species, D and A, are adopted as the starting point. It is, however, important to take into account the structural differences occurring between ion, D^+ or A^- , and the parent molecule, D or A. This is specially remarkable in the case of the amino groups, $-NR_2$, with a pyramidal (sp^3) hybridisation, frequently met as donors, which in form of the $-NR_2^+$ ions turn to be planar (sp^2).

The molecular structures of the equilibrated (relaxed) excited CT states are or become accessible to experimental study by measuring of, e.g., the value and orientation of the transition moments in absorption and in emission; band widths and Stokes' shifts; time-resolved electronic and vibrational absorption spectra. Much information is also gained by comparison of the studied excited state behaviour to that of the suitably tailored model molecules (e.g., [3]).

INTERMOLECULAR EXCIPLEXES

EDA complexes

Direct comparison of the ground- and excited state structures is possible for the weak electron donor-acceptor (EDA) complexes existing already in the ground state. In the long known examples, e.g., benzene (or toluene) + tetracyanobenzene [4,5], the ground state complex roughly corresponds to the maximal overlap of the orbitals involved in the CT interaction, as required by the Mulliken's theory of weak EDA complexes [6]. In the excited CT state, mutual Coulombic attraction of D^+ and A^- brings the opposite charges to close approach, which corresponds to a full geometrical overlap (Fig.2). For symmetry reasons, however, it is the zero orbital overlap geometry: $\langle d|a' \rangle = 0$ in the notation of Beens and Weller [2] (in this notation $HOMO(D) \equiv d$; $LUMO(D) \equiv d'$; and analogously for A); the excited state is represented by a practically pure CT configuration, with a symmetry- (and overlap-) forbidden fluorescence transition [7].

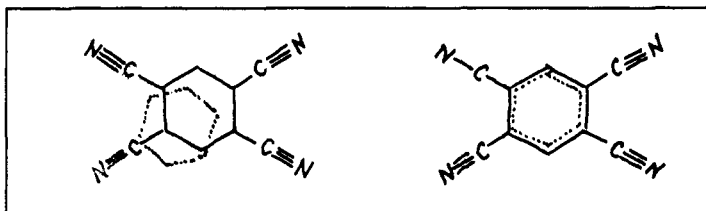


Figure 2. Tetracyanobenzene + benzene complex. Left: in the ground state; right: in the relaxed CT state. After Nagakura al. [4].

'True' exciplexes

In the case of typical intermolecular exciplexes the ground state is repulsive; only the excited state has a definite minimum on its potential hypersurface.

The admirably thorough calculation has been performed for the system: diethylaniline + anthracene [2]. The optimum geometry of the CT state (Fig.3a) is that with nearly pure CT configuration and maximal Coulombic interaction. There are some nonzero overlap integrals (albeit small, ~ 0.01 , due to a considerable interplanar distance of $\sim 3 \text{ \AA}$): $\langle d|a' \rangle$ is responsible for mixing with the ground state; $\langle d'|a' \rangle$ - with the locally excited state D^* .

The transient absorption spectra of this and analogous exciplexes reflect indeed the presence of both types of transitions, those characteristic of ions A^- and D^+ , and the reverse electron transfer transitions to the locally excited levels of D^* or A^* [8,9].

With the locally excited states (D^* or A^*) energies approaching to the zero order CT level, the interaction increases, lowering the energy of the excited state, and lowering the value of its dipole moment. By suitably changing D and A one can observe a continuous change from full ET (pure CT) states to nonpolar excimers.

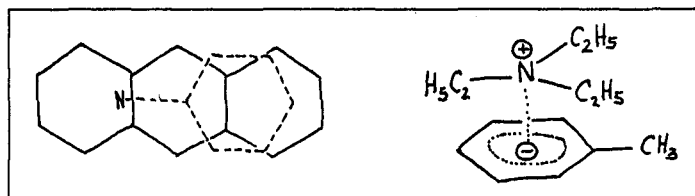


Figure 3. Calculated equilibrium structures of intermolecular exciplexes. Left: anthracene + diethylaniline (according to [2]); right: toluene + triethylamine (according to [10]).

With increasing polarity of the solvent the rate of dissociation of intermolecular exciplexes into free (solvated) radical-ions increases; in strongly polar solutions the exciplexes are, as a rule, not observable; the absorption spectra of free ions appear instead [11,12].

Aliphatic amines form exciplexes with numerous aromatic systems. As the donor properties are localized on the N atom, and the locally excited D^* states are high above the CT state, the molecular structure corresponds rather well to that predictable in a qualitative way. An example is shown in Fig.3 (b): the N atom lies of the amine (donor) over the centre of aromatic (acceptor) ring. Due to the symmetry and zero overlap integrals it is a pure CT state; it is located, however, in a broad energy minimum; hence, it can be easily contaminated by thermal motions either with the local A^* state or with the ground state, AD [10].

INTRAMOLECULAR BRIDGED EXCIPLEXES

An "insulating" bridge, usually formed by a system of σ -bonds and saturated carbon atoms, can link the D and A moieties. In the most studied systems it has been the polymethylene chain: $D-(CH_2)_n-A$. In the ground state the conformation has in general no definite correlation of D and A; After the (local) excitation of either D or A, the ET occurs if the reactants are not too far away, and then - due to operation of the harpooning effect - an exciplex is formed. Here again, the insight into its structure can be achieved either by theoretical approach, or by experimental means, usually from the time-resolved electronic absorption spectra [8,13,14].

In all cases there is a tendency to achieve the geometry which has been found optimal in the case of inter-molecular exciplexes. The strains imposed by the conformation of the bridge usually limit the freedom of mutual spatial adjustment of the radical ion moieties, D^+ and A^- . Best known is the *Hirayama rule* [15], stating that from among the aromatic polymethylene-bridged systems the most stable sandwich structure is that with $n=3$. In the case of very short chains ($n=1$ or $n=2$) the absorption spectra indicate the existence of a CT structure (ionic bands), at $n=3$ the broader and more complex exciplex bands appear [13,14].

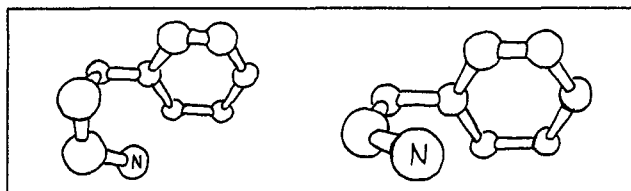


Figure 4. Flexible intramolecular exciplexes; Left: phenyl- $(CH_2)_2-NMe_2$ ($n=2$); right: phenyl- $(CH_2)_3-NMe_2$ ($n=3$) (after [10,17]).

It is somewhat different in the case of aliphatic amines as donors bound by a polymethylene chain: at $n=3$ there is still a strain, and - specially for the larger aromatic acceptors - the optimal geometry cannot be achieved [16,17]. For the simplest aromatic acceptor, benzene, the schematic views of the calculated structures are shown in Fig.4. For $n=2$ the amine N atom lies over or close to the nodal symmetry plane of the ring; some overlap integrals disappear, and the interaction with the local excited states is weak. For $n=3$, the less symmetric structure leads to interactions, which stabilize the exciplex.

In strongly polar solvents the flexibly bridged exciplexes change their structure due to solvation; the A^- and D^+ ions cannot, however, diffuse away. They remain bonded, with a distribution of conformations usually referred to as the *stretched* conformation. It is still able to emit fluorescence, and its absorption spectrum is that of the ions.

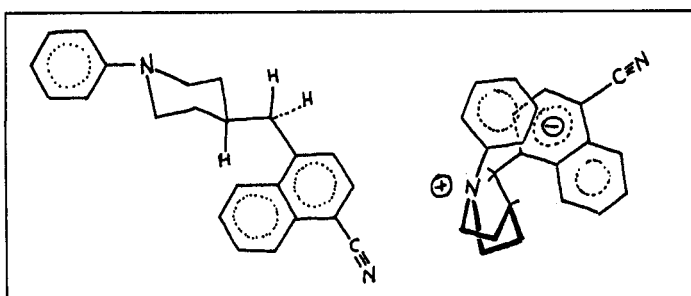


Figure 5. Intramolecular exciplex with limited rigidity of the bridge: after ET, the piperidine ring *chair-to-boat* conversion folds the molecule [18].

Limited rigidity is found with, e.g., saturated six-membered piperidine ring (Fig.5), where the stretched molecule undergoes - even in a free molecular jet - a harpooning and folding to the exciplex structure most stable in vacuum or in weakly polar solvents [18a]. In strongly polar solvents it is the stretched (chair) conformation, with its large dipole moment, which is the most stable [18b].

In the case of a rigid bridge (Fig.6) the molecule seems not to change markedly its skeleton in the CT state. Best known are the long rigid spacer $D \equiv A$ molecules [18,20] (Fig.6, left). The longest one is drawn in the Figure (bottom, left). They exhibit huge dipole moments, up to 70 D [21]. Leaving here aside the fascinating topics of the $\pi\sigma$ and long distance through-bonds interactions, operating in the radiative and

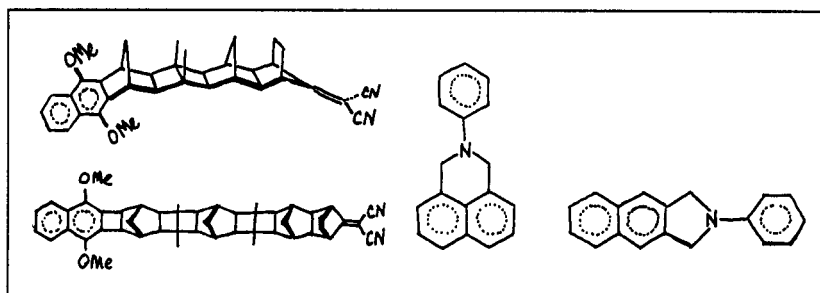


Figure 6. Rigidly bridged intramolecular CT states. Left: long rigid spacer $D \equiv A$ molecules [18b,19]; right: doubly bridged dialkylaniline-naphthalene systems [20].

thermal ET, the lack of any direct $\pi\pi$ overlap (due to the distance between D and A) implies practically pure CT states in these compounds.

In the rigidly bonded dialkylaniline-naphthalene systems [20] (Fig.6) the dipole moment values, corresponding to nearly full separation of charges, demonstrate the approximate purity of the CT state. In these cases it may be due both to the distance, and to the symmetry.

TWISTED INTRAMOLECULAR CT STATES (TICT)

If D and A are singly bonded, D-A, there is only one degree of freedom left for mutual adjustment of both moieties: that of internal rotation. It has been found that the compound **1** (Fig.7) emits two fluorescence bands, the lower energy band originating in a highly polar state [22]. It has been recognized later that the internal ET is accompanied by an internal rotation [23a]; for the resulting CT state the term *Twisted Intramolecular CT State (TICT)* has been coined [23b]. Large number of compounds with very different D or A moieties are shown (or suspected) to form the TICT excited states (for reviews: e.g.[23c,24]).

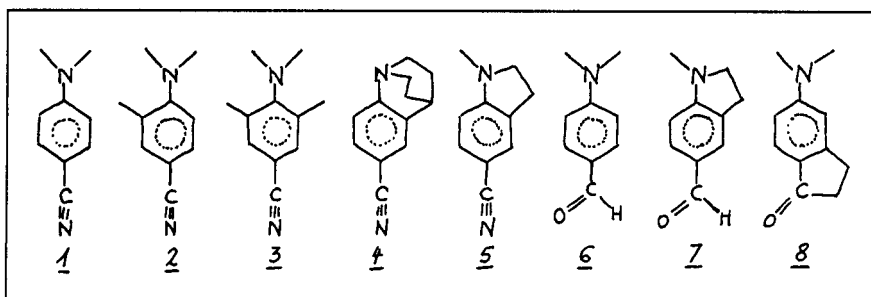


Figure 7. **1** and **6** - typical TICT forming D-A molecules. Others: model compounds, sterically hindered or with fixed conformation (see text).

Model compounds for the CT state of **1**, with a strong steric hindrance against coplanarity of D-A (**2,3**) or fixed 90° twisted configuration (**4**), exhibit only the CT emission; that with amino group fixed in the molecular plane (**5**) - only the "normal" fluorescence. Similarly with **6**: comparison of its behaviour with that of **7** and **8** proved it is the amino group rotation which models the CT state.

TICT state of **3** is formed even in the gas phase or in molecular jet [25]. In the case of **2** or 4-dialkylamino-5-methyl-pyrimidines the steric effect of *o*-CH₃ makes the formation of the TICT state possible in the Van der Waals complexes in molecular supercooled jet [26].

The identity of picosecond time-resolved absorption of **1** and **6** in polar solvents with the spectra of constituent radical ions, A⁻ and D⁺, gave a proof of the TICT structure [27] as A⁻-D⁺, with practically unperturbed ionic spectra, i.e., with zero overlap between the π orbitals of D and A. In contrast to sandwich exciplexes, the electronic structure of the polar state virtually does not change in nonpolar and polar media; the ions cannot diffuse away; the CT state is more and more stabilized with the increasing polarity of the surroundings.

The overlap and admixture of other states to the CT state increase with aromatic donors instead of aliphatic amines, and with aromatic acceptors larger than benzene. It is reflected in the absorption spectra of the TICT state; they correspond no more to the simple sum of absorptions of D⁺ and A⁻ (e.g., [28]). The mixing of the CT and nonpolar states (here also the excitonic states) manifests itself in lowering of the dipole moment, μ^* , and in the increase of the emission rate, k_f .

These effects are specially marked in *biaryls*, where the ET is accompanied by a symmetry breaking in the originally nonpolar molecule (e.g., [24,29]).

We can expect new types of exotic CT structures to be found in more complex molecules, and particularly in supramolecular systems, also in biological macromolecules and in the efficient natural ET systems.

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