

## Straight, bent and twisted intramolecular charge separated states as seen by time-resolved microwave conductivity (TRMC)

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### Abstract

The application of the TRMC technique to the study of non Franck-Condon charge separated states formed subsequent to vertical photo-excitation is illustrated with examples which include long-distance intramolecular electron transfer and molecular folding or twisting.

### INTRODUCTION

The absorption of light by molecules is invariably accompanied by a change in the spatial distribution of the bound electrons. For some molecules this can result "immediately" in a large change in dipole moment in the Franck-Condon excited state. For others rearrangements of the electrons and/or nuclei occur subsequent to vertical excitation which induce or accentuate charge separation. This secondary development of dipolar character is the topic of the present paper. In particular we hope with a few examples to illustrate the insights into this type of process that the time-resolved microwave conductivity (TRMC) technique can provide.

While we will not deal directly with the TICT concept in this paper, we acknowledge that this has been a powerful driving force in the study of molecular charge separation processes. This brainchild of professor Grabowski has without doubt functioned as a vital, stimulating essence in the development of whatever understanding we have about the idiosyncracies of excited molecules. For his scientific insight and his personal effort and determination we express our warm admiration.

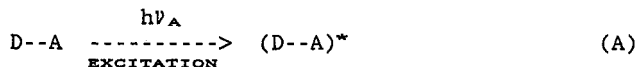
### EXPERIMENTAL

In the TRMC method (ref. 1) the molecule of interest is photo-excited by flash-photolysis of a dilute solution in a non-dipolar solvent. The solution is contained in a microwave cavity. Any change in the dielectric loss of the solution on photolysis results in a change in the power reflected by the cavity. This is monitored with nanosecond time-resolution thus allowing the detection of transient changes in loss resulting even from the formation of short-lived singlet states.

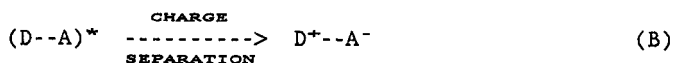
The solutions of absorbance  $ca\ 1\ cm^{-1}$  and are purged with  $CO_2$  to remove air and suppress any mobile electrons which might be formed in low-yield multiphoton ionisation processes. The 308 nm XeCl line of an excimer laser is used with an incident power at the cell of  $ca\ 10\ mJ/cm^2$ . Single pulses are used with the capability of averaging up to 64 traces. The microwave circuitry has been described fully elsewhere (ref. 1). The time resolution is limited by the pulse width of  $ca\ 7\ ns$  and the response time of the cavity of  $ca\ 5\ ns$ . Both are known accurately so that lifetimes down to  $ca\ 3\ ns$  can be estimated directly. For shorter lifetimes an independent measurement is necessary if quantitative estimates of dipole moments are to be made.

## RESULTS AND DISCUSSION

In what follows we will be concerned with molecules which subsequent to photo-excitation form a state which involves a large degree of charge separation and often in addition a large change in conformation compared with the ground state. We will denote the ground state of these molecules by D--A with D a donor moiety, A an acceptor moiety and the double hyphen representing a hydrocarbon spacer separating the active sites. Photo-excitation is considered to lead initially to the lowest excited state in the singlet manifold(s) found in absorption of the molecular assembly according to Kasha's rule. For weak electronic coupling through the spacer unit this is usually the S<sub>1</sub> state of either the locally excited donor (LED) or acceptor (LEA). For strong coupling, as for example with conjugated spacers, the initial state may be a combined electronic state of the whole molecular assembly. The symbol (D--A)\* is taken to represent in general the "initial" state which for the molecules considered is only weakly dipolar if at all.



Secondary charge separation is indicated by + and - suffixes e.g.



In certain cases (B) may involve the transfer of less than a whole electronic charge.

Two qualitatively different conformational changes of the molecule are considered: folding which is represented by



and twisting by



The former results in longitudinal displacement and hence closer approach of the active sites while the latter involves a rotational displacement with no substantial change in D to A distance.

In what follows we will present examples of molecules for which the above processes play an important role in their photophysics and illustrate how this is reflected in the TRMC transients that are observed.

### Long-distance electron transfer: rigid $\sigma$ -bond spacers

In recent years it has become increasingly accepted that rapid charge separation can occur between donor and acceptor moieties separated by distances much larger than their van der Waals diameter even in the absence of a conjugated  $\pi$ -bond spacer. The evidence for this has come from the study of D--A compounds with rigid, sigma bonded spacers such as those synthesised by one of the present authors (M.N.F-R) 4 of which are shown in Fig. 1. The three-dimensional, norbornyl-type spacing units in these compounds restrict both the relative longitudinal and rotational motion of the donor and acceptor moieties.

Convincing evidence that long-distance electron transfer occurs subsequent to photoexcitation of the donor moiety of these compounds was provided by the TRMC transients shown in Fig. 1. From the magnitudes of the transients the dipole moments of the intermediates responsible could be estimated to increase from 26 D for the shortest to almost 70 D for the longest (ref. 2). These values are slightly larger than those expected for complete electron transfer over the length of the intervening spacer which varied from 4.6 to 11.5 Å. Also, the lifetimes of the charge separated states are clearly seen to increase markedly with increasing distance. From a full kinetic analysis of the traces decay times of 1.0, 6, 32 and 360 ns are determined. These correspond to a close to exponential dependence on distance as would be expected for long-distance tunnelling recombination.

Companion fluorescence experiments (refs. 3,4) have shown that the rate of the charge separation step is also exponentially dependent on distance for these compounds with even for the longest a separation time of only 140 ps, i.e. a factor of almost 3000 faster than the recombination step. Even for a driving force for charge separation of only a few hundred millivolts and in completely non-polar solvents the separation process is found to proceed with close to its maximum rate.

These results are particularly important in further discussions of intramolecular charge separation since they leave little doubt that long-distance electron

transfer can occur through an extensive  $\sigma$ -bonded "barrier" if it is energetically feasible and if it can compete with other decay processes.

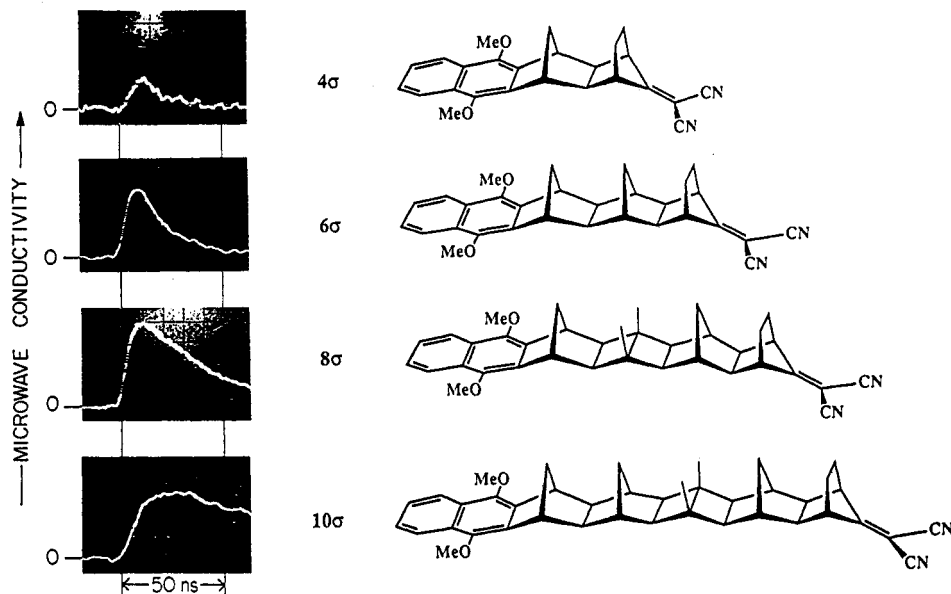
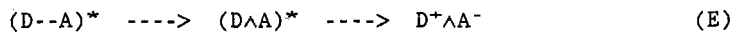


Fig. 1. Transient changes in the microwave conductivity on flash-photolysis of benzene solutions of the compounds shown (from *Nature*, **320**, 615 (1986)).

#### Folding-induced charge separation; flexible $\sigma$ -bond spacers

A large body of research has been carried out on the photoexcitation of D-A compounds for which the bridging unit is an oligo-methylene chain. The results have indicated the formation of states which resemble very closely, in their optical properties, those of the sandwich-type,  $\pi$ - $\pi$  exciplexes of the same, non-bonded donor and acceptor molecules. This has been attributed to initial local photoexcitation of the donor or acceptor moiety being followed by conformational diffusion within the flexible methylene chain resulting in a statistical close encounter of the D and A extremities. Short-range electron transfer can then occur to form the dipolar exciplex in the folded configuration.



Strong evidence for this mechanism was found for certain D-A systems in the form of a viscosity dependence of the growth of the exciplex-type fluorescence (refs. 5-7). What has become a classic molecule in this respect is the trimethylene assembly of pyrene and dimethylaniline,  $1\text{Py}(\text{CH}_2)_3\text{DMA}$  which displays a viscosity dependent growth of exciplex emission over a timescale of nanoseconds in saturated hydrocarbon solvents at room temperature.

If the mechanism represented by (E) is correct then one should observe on photolysis of  $1\text{Py}(\text{CH}_2)_3\text{DMA}$  using the TRMC technique initially a negligible change in dielectric loss corresponding to local excitation of the pyrene moiety. An increase in loss should subsequently occur as the dipolar exciplex state is formed with molecular folding as the rate controlling step. This delayed growth of the TRMC transient is in fact observed as is shown for a trans-decalin solution of  $1\text{Py}(\text{CH}_2)_3\text{DMA}$  in Fig. 2A. Both the rate of growth and decay of the TRMC signal match very closely those found for the fluorescence attributed to the folded exciplex state. For example in *n*-hexane ( $\eta = 0.31$  cP) and trans-decalin ( $\eta = 2.2$  cP) the mean lifetimes for growth of the TRMC transient are 4.5 and 11 ns. These values are similar to the 4 and 8 ns found in the early fluorescence work (refs. 5,6) and 4.1 and 9.7 ns determined more recently using time-correlated single photon counting (ref. 8). The pronounced temperature/viscosity dependence found in the fluorescence studies is also apparent in the TRMC transients as shown in Fig. 2A.

The TRMC results therefore provide conclusive evidence that mechanism (E) is operative for  $1\text{Py}(\text{CH}_2)_3\text{DMA}$  in hydrocarbon solvents and in particular that rapid, long-distance electron transfer does not occur in the outstretched configuration but

requires considerable conformational rearrangement. The dipole moment of the folded exciplex is estimated from the TRMC data to be  $13 \pm 2$  Debye.

The situation is apparently more complex in polar solvents for which much more rapid development of exciplex fluorescence is observed. This is also found to be the case in TRMC measurements on  $1\text{Py}(\text{CH}_2)_3\text{DMA}$  in the pseudo-polar solvent para-dioxane. This is illustrated in Fig. 2B which shows the dipolar transient to grow-in much more rapidly in the latter solvent than in trans-decalin despite their similar viscosities. Two explanations can be put forward: either rapid electron transfer occurs in an outstretched chain configuration and is followed by fast folding to give the exciplex, a process known as "harpooning" (ref. 9); or a large percentage of folded configurations is already already present in the ground state. The former possibility would not be in conflict with the conclusion based on the results in the previous section if long-distance electron transfer for  $1\text{Py}(\text{CH}_2)_3\text{DMA}$  was energetically unfavourable in saturated hydrocarbon solvents but allowed in more polar media. However in  $^1\text{H}$ NMR measurements on  $1\text{Py}(\text{CH}_2)_3\text{DMA}$  an appreciable ring current effect caused by the mutual overlap between the DMA and Py moieties is observed (ref. 8) indicating the mean distance between the end groups to be smaller than that in the configuration with an all-trans trimethylene chain. This topic will be discussed more fully in a future publication.

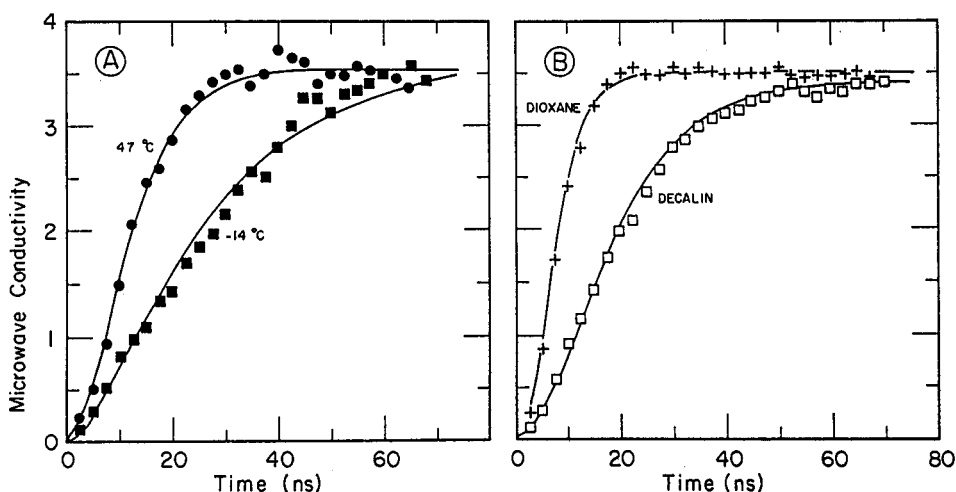
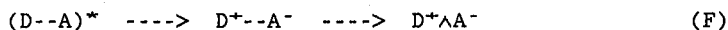


Fig. 2. Growth of the microwave conductivity on flash-photolysis of  $1\text{Py}(\text{CH}_2)_3\text{DMA}$ : (A) trans-decalin solvent at 47 and  $-14^\circ\text{C}$ ; (B) trans-decalin and dioxane solvents at room temperature. The data points have been divided by the decay function  $\exp(-t/\tau_d)$  found at long times for which  $\tau_d$  was ca 90 ns.

#### Coulomb-induced folding; semi-rigid $\sigma$ -bond spacers

The first evidence, based on TRMC measurements (ref. 10), that harpooning, represented by (F), can occur for semi-rigid D-A compounds was found for the compound DMA[5]NpCN the structure of which is shown in Fig. 3.



This took the form of transients in saturated hydrocarbon solutions which indicated the rapid, subnanosecond formation of a highly dipolar product of photolysis which subsequently decayed over a timescale of several nanoseconds to yield a longer-lived, but less dipolar species. An example of such a biexponential TRMC transient is shown in Fig. 3. While the final decay was found to be solvent independent with a lifetime of approximately 70 ns, the initial decay displayed a solvent dependent decay time which increased with increasing viscosity and decreasing temperature. A TRMC signal of similar initial magnitude was observed in para-dioxane but in this pseudo-polar solvent the decay was found to be simple mono-exponential.

Confirmation that the two species involved in the saturated hydrocarbon solutions were both singlet states of the solute was provided by parallel fluorescence measurements (ref. 10) which showed two emission bands both bathochromically shifted with respect to the quenched LEA fluorescence. The shorter wavelength band of the two

decayed with a lifetime identical to the initial decay of the TRMC transient under the same conditions of solvent and temperature to yield the more red-shifted band with a decay time of ca 70 ns. In addition, the spectrum of the final emission resembled closely that found for the intermolecular sandwich exciplex of 1-cyano-naphthalene and *N,N*-dimethylaniline found in *n*-hexane.

These combined results suggest that in alkane solvents electron transfer between D and A is energetically feasible in the outstretched configuration of DMA[5]NpCN and occurs on a subnanosecond timescale to be followed on a timescale of nanoseconds at close to room temperature by folding-up of the molecule under the influence of the coulomb force as illustrated in Fig. 3. It is worth noting that this requires inversion of the piperidine ring. The dipole moment has been estimated to decrease by a factor of at least 1.7 on folding (ref. 10). In more polar media the outstretched configuration of the charge separated state is apparently preferentially stabilised by solvation and by the reduction in the coulomb force which is necessary to overcome the barrier to ring-inversion.

Molecular beam experiments (ref. 11) on DMA[5]NpCN have substantiated the occurrence of the harpooning phenomenon for this molecule even in the gas phase. Other examples of semi-rigid D-A molecules which undergo folding subsequent to photoexcitation have also been found (ref. 12).

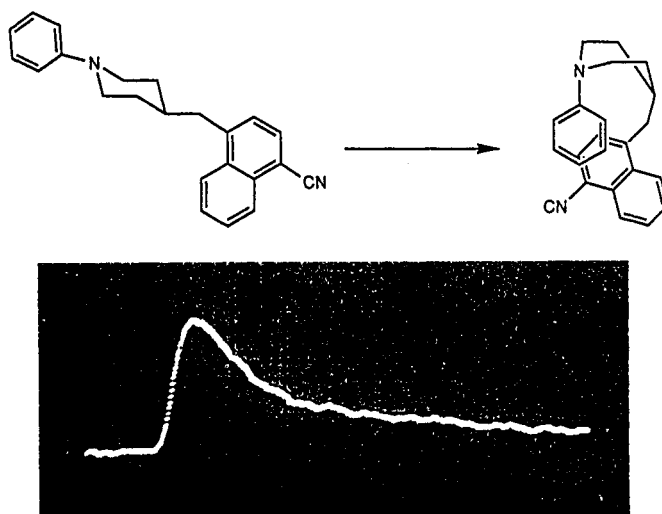


Fig. 3. Biexponential decay of the microwave conductivity of a solution of the compound shown above in *trans*-decalin at  $-20^{\circ}\text{C}$  (total time 200 ns).

#### Twisting-induced charge separation; $\pi$ -bond spacers

The induction of (increased) intramolecular charge separation by mutual rotation of component parts of a molecule, as represented by (G), is a topic fraught with controversy whether it comes under the heading of "sudden polarisation" involving rotation about an ethylenic double bond or "TICT" involving more subtle rotary motions of individual chromophoric units.



We restrict the contribution of TRMC in this area to recent results on the zwitterionic nature of the twisted excited state of symmetrical ethylene derivatives.

Evidence that the relaxed excited singlet state of tetraphenylethylene (TPE) is highly dipolar is shown in Fig. 4 by the readily measureable change in dielectric loss that occurs on flash photolysis of a cyclohexane solution. The much smaller transient found for a benzene solution is in agreement with optical absorption (refs. 13,14) and optical calorimetry (ref. 15) studies which show a marked decrease in the lifetime of the  $^1\text{p}^*$  state of TPE with increasing  $E_{\text{T}}(30)$  of the solvent.

The TRMC signal is found to be independent of viscosity in alkane solvents indicating that dipole relaxation is not determined by molecular rotation or by large conformational changes but most probably by interconversion between the two degenerate zwitterionic states. If the timescale of interconversion is approximately 10 ps,

as might be expected on the basis of results obtained for bianthryl (ref. 16), then the dipole moment of the twisted excited state of TPE is found to be  $8 \pm 1$  D.

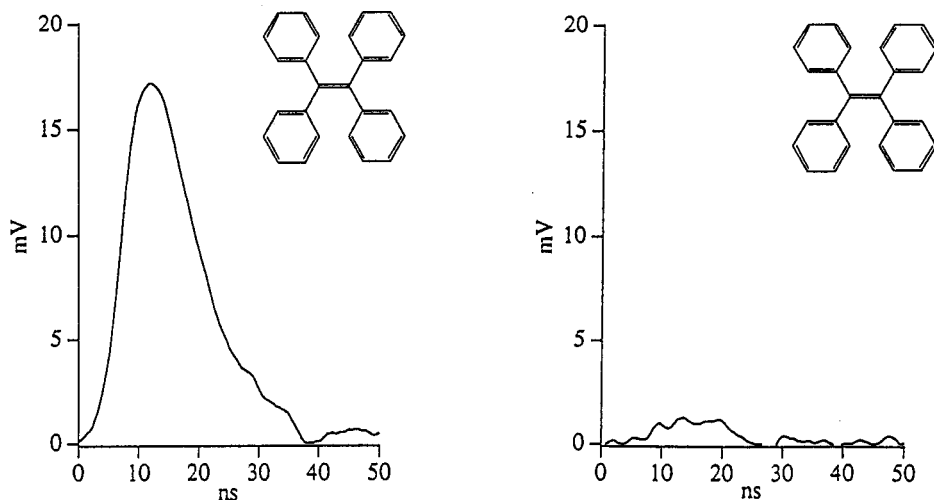


Fig. 4. TRMC transients found on flash photolysis of solutions of tetraphenylethylene in cyclohexane (left) and benzene (right).

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