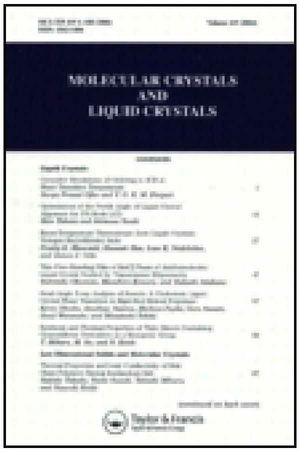

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Time-Resolved Microwave Conductivity Studies of Long-Distance Electron Tunnelling in Molecular Systems

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TIME-RESOLVED MICROWAVE CONDUCTIVITY STUDIES OF LONG-DISTANCE ELECTRON TUNNELLING IN MOLECULAR SYSTEMS

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Abstract Recent results on charge recombination via electron tunnelling through intervening saturated hydrocarbon media, obtained using the time-resolved microwave conductivity (TRMC) technique, are presented. The systems studied are a) isolated donor-insulator-acceptor molecules (DIADs) with rigid, saturated hydrocarbon spacers of variable length and b) columnar aggregates of octa-*n*-alkoxy substituted phthalocyanines. In both cases the rate of recombination of charge is found to depend exponentially on the dimension of the intervening saturated hydrocarbon medium i.e. $k_R = \nu \exp(-aR)$, with a = 0.88 and 0.64 $Å^{-1}$ respectively.

INTRODUCTION

Long distance, intramolecular or intermolecular electron tunnelling through insulating hydrocarbon barriers is the basis of many recent suggestions for the construction of molecular opto-electronic and energy-storage devices. Essential to the sensible synthesis of such molecular devices is an understanding of the factors which control the dynamics of the charge separation and charge recombination processes. This will include the thickness and (chemical) nature of the barrier, the dielectric properties of the bulk medium and the driving force for forward and backward electron transfer. We have recently applied time-resolved microwave conductivity (TRMC) techniques to this problem area using specially synthesised molecular model systems together with nanosecond flash-photolysis and pulse-radiolysis sources of excitation and ionization.

The TRMC method can provide a quantitative measure of small changes which occur in the microwave conductivity (dielectric loss), $\Delta\sigma(\omega)$, of materials when subjected to a short pulse of radiation[1-3]. The conductivity can result from the formation of free charge carriers (ionization), in which case the microwave conductivity is related to the concentration of the carriers, N_i, and their mobilities, $\mu(+)$ and $\mu(-)$, by

$$\Delta\sigma(\omega) = eN_i[\mu(+) + \mu(-)] \qquad (1)$$

or from dipolar species (intramolecular charge separation) in which case the conductivity change is related to the concentration of dipolar species formed, N_d, their dipole moment, p, and rotational relaxation time, t_r, by

$$\Delta\sigma(\omega) = N_d(\varepsilon + 2)^2 p^2 F(\omega t_r)/[27 k_B T t_r] \qquad (2)$$

Information on the charge carrier mobilities or the dipole moments respectively of intermediates can be derived from the end-of-pulse magnitudes of the TRMC transients and information on the dynamics of charge recombination can be derived from the relaxation kinetics of the transient conductivity change. The results in the present manuscript will be restricted to the latter aspect.

INTRAMOLECULAR CHARGE RECOMBINATION

The structures of the compounds used to study the effect of distance on long distance intramolecular charge recombination are shown in figure 1 apart from the compound for which the donor, dimethoxynaphthalene, and acceptor, dicyanoethylene, are separated by 13 sigma bonds.

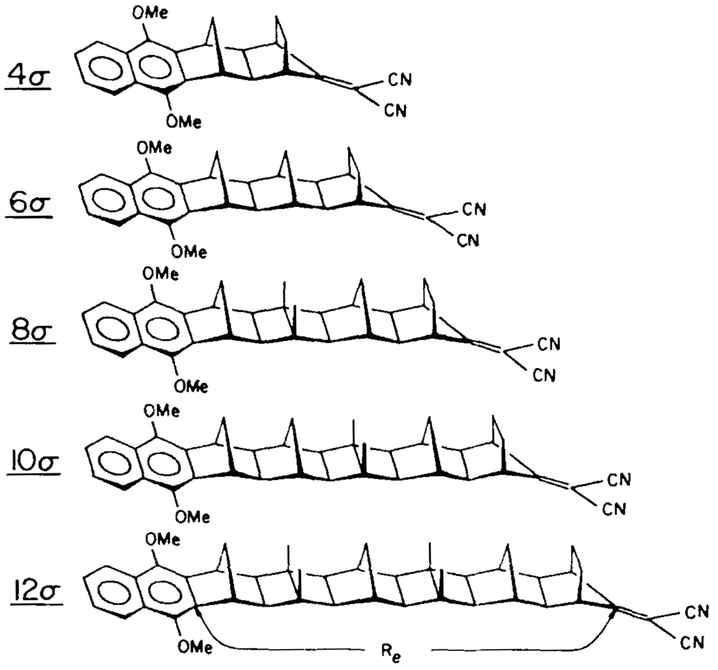

FIGURE 1 The molecular structures of the donor-insulator compounds used in the present work and referred to in the text by the number of intervening sigma bonds.

The compounds are referred to in the text in terms of the number of sigma bonds separating the donor and acceptor. As can be seen the structures are completely rigid which prevents both relative lateral and rotational movement of the donor and acceptor moieties. The edge-to-edge distances between D and A, R_e as shown in figure 1, have been determined from X-ray diffraction analysis of the solids[4,5] and increase from 4.6 to 14.6 Å from the 4σ to the 13σ compound.

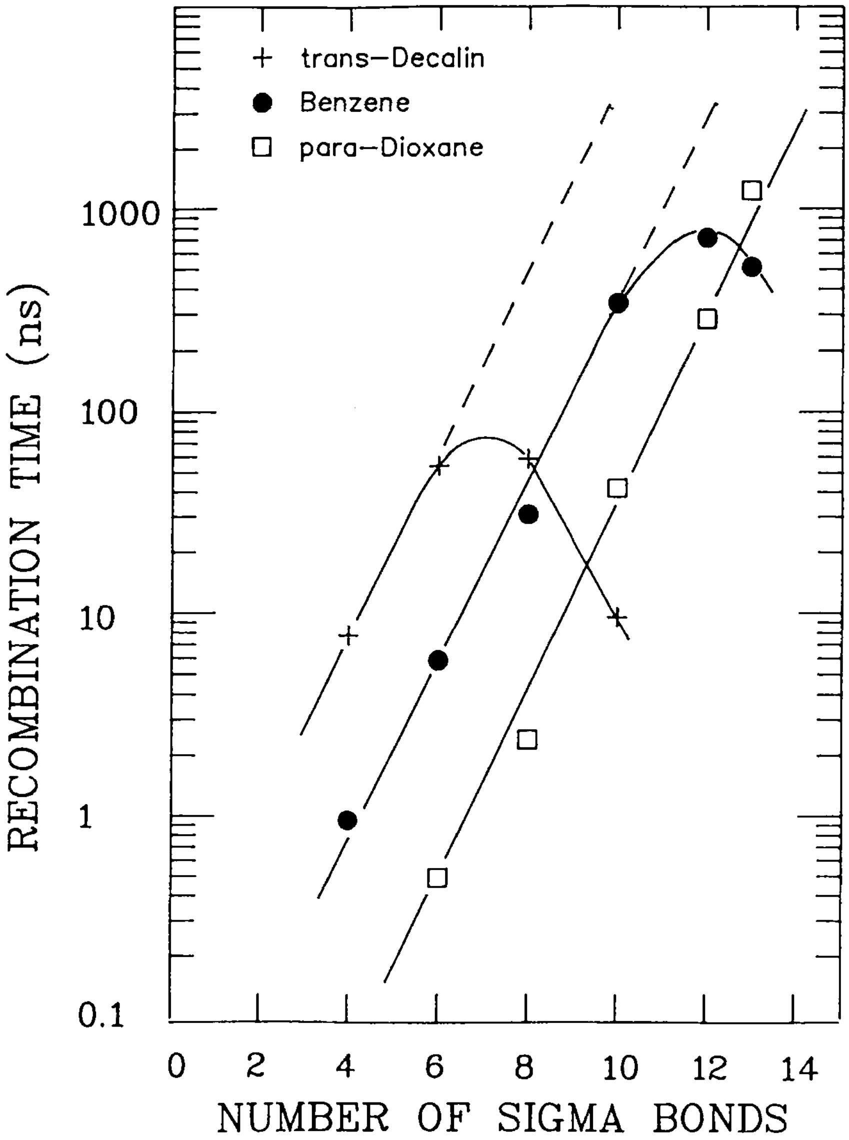

FIGURE 2 The charge recombination times determined for the compounds shown in figure 1 in the solvents trans-decalin, crosses; benzene, filled circles; and para-dioxane, open squares.

The compounds were locally excited, at the donor dimethoxynaphthalene site, by flash photolysis of dilute solutions (*ca* 10^{-4} M) in the non-polar solvents trans-decalin, benzene or para-dioxane. The excitation wavelength was 308 nm (XeCl line of a Lumonics HyperX 400 excimer laser). The design of the cell and detection equipment has been described fully in a previous publication[2]. Transient digitizer traces of the TRMC transient signals observed have also been published previously[4,6] together with calculated values of the dipole moments of the fully charge separated, giant dipole intermediates which are formed by rapid (subnanosecond) electron transfer from donor to acceptor subsequent to excitation[4,7,8].

In figure 2 the decay times of the TRMC transients, corresponding to lifetime towards charge recombination, are plotted against the number of sigma bonds in the hydrocarbon bridge, N_s, for the three solvents studied. In addition to being markedly dependent on thelength of the hydrocarbon bridge, as might be expected, the recombination process is seen to be extremely sensitive to the nature of the surrounding medium, as pointed out previously[4,9]. It is worth pointing out that the dielectric constants of the three solvents are very similar, 2.17, 2.28 and 2.15 respectively. Benzene and dioxane have however been found to decrease the energy level of charge separated states, compared with a saturated hydrocarbon, by approximately 0.3 and 0.6 eV respectively. Perhaps surprisingly the recombination process, at least for the shorter compounds, appears to be much faster in the more solvating medium dioxane than in the saturated hydrocarbon solvent. While this goes against intuitive feelings that ionic species should be least stable in saturated hydrocarbon liquids, it does, at least qualitatively, agree with the predictions of electron transfer theory for highly exothermic reactions[10,11] which should display an increasing rate with decreasing exothermicity, the so-called "inverted region" of Marcus theory.

As can be seen in figure 2, the recombination lifetime for the three solvents seems to obey the same exponential dependence on distance initially, i.e. for the shortest compounds, as shown by the parallel straight lines drawn through the points. This distance dependence is given in terms of the rate by

$$k_R = \nu_R \exp(-1.0N_s) \qquad (3)$$

where N_s is the number of sigma bonds separating donor and acceptor. When translated into a distance dependence on the basis of an average value of 1.14 Å per sigma bond[4,5] this gives

$$k_R = \nu_R \exp(-0.88R) \qquad (4)$$

for R in angstrom.

Clearly equations (3) and (4) break down for large separations in trans-decalin and for somewhat longer distances for benzene. Thus the lifetime goes through a maximum and then decreases rapidly with further increase in distance. The fact that these deviations from the exponential increase expected are accompanied by the observation of delayed donor fluorescence with a lifetime equal to that of the decay of the TRMC transient strongly support the argument that the effect is due to the occurence of recombination no longer directly to the ground state, but via back electron transfer to give the locally excited donor. This recombination pathway is given in the reaction scheme shown in figure 3 as (4) followed by (2). Clearly in order for this pathway to occur the energy levels of the local excited donor and the charge separated state must be quite close to being degenerate. It is worth pointing out that under these conditions the rate of recombination has been found to be sensitive not just to the solvating power of the medium but also to the polarisability with quite large differences in kinetics even between the two saturated hydrocarbons n-hexane and trans-decalin[9].

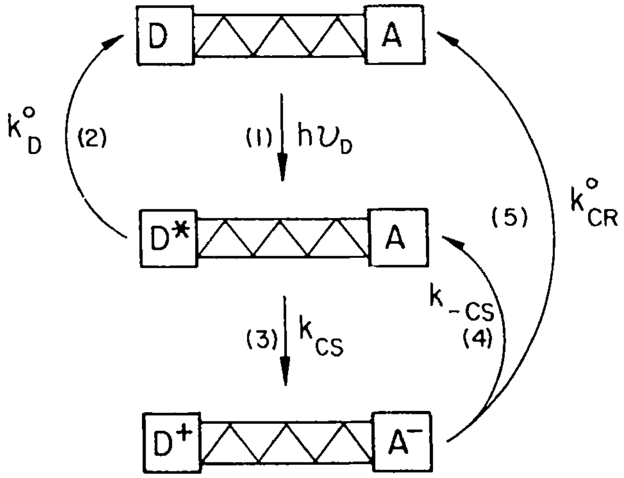

FIGURE 3 A reaction scheme describing the processes occurring subsequent to photoexcitation of the compounds shown in figure 1.

The occurrence of "back-transfer recombination" only for the longer molecules results from the fact that, because of the low dielectric constants involved, the charge separated states increase quite substantially in energy content as the donor acceptor distance increases due to the decrease in the coulombic potential energy. This is illustrated in figure 4 for benzene as solvent.

From the present results it may be concluded that if one wishes to maximise the energy content <u>and lifetime</u> of a rigid charge separated state then this can best be accomplished in a medium with no polar interaction with the charge centres. For charge separation to occur at all and in particular if back-transfer is to be minimised, the driving force should be at least 0.2 eV. It is possible however that these conclusions are only valid for the particular norbornane-type spacer used in the present study.

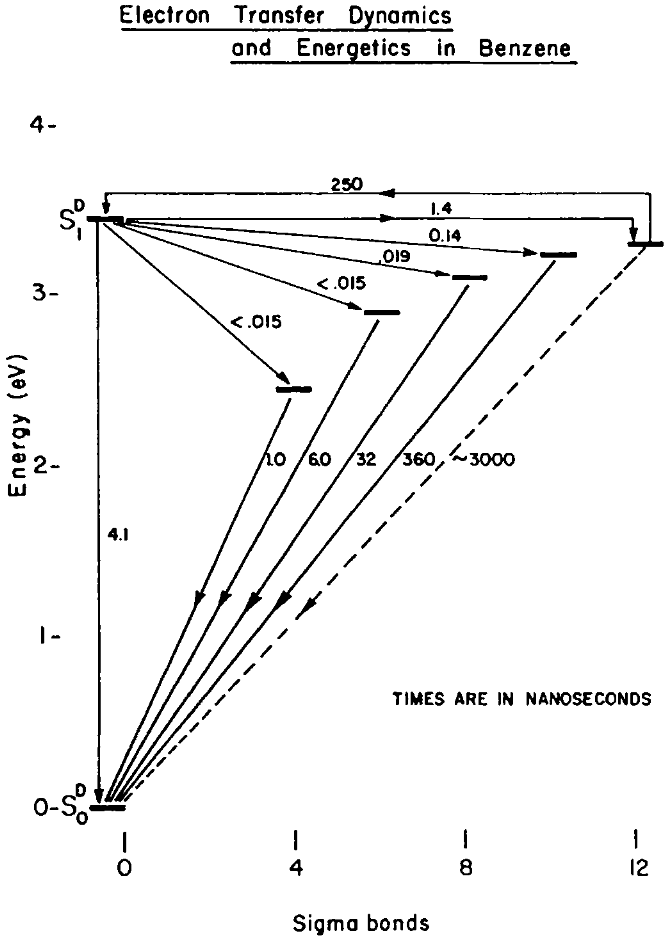

FIGURE 4 A schematic diagram to illustrate the increase in energy level of the charge separated state with increasing length of the compounds shown in figure 1 in benzene together with the kinetic consequences for charge recombination.

INTERMOLECULAR CHARGE RECOMBINATION

Peripherally octa-*n*-alkoxy substituted phthalocyanines (with alkyl chain lengths of C_6 or longer) have been found to form an ordered, columnar mesophase at elevated temperatures[15,16] as illustrated in figure 5.

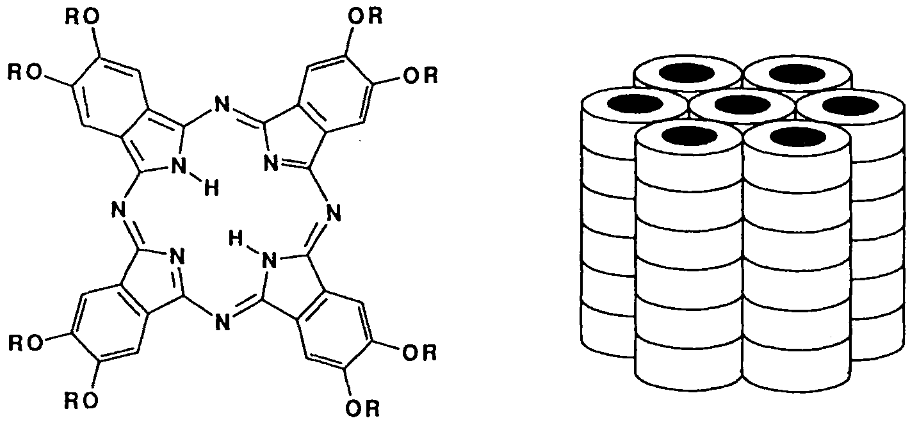

FIGURE 5 The molecular structure of the octa-*n*-alkoxy substituted phthalocyanine derivatives studied in the present work, with n = 1, 6, 9 and 12. On the left is an illustration of the ordered columnar arrangement found in the liquid-crystalline mesophase of the three longest compounds.

From X-ray diffraction patterns it can be seen that the distance between the phhtalocyanine (Pc) moieties within the columns is well defined and equal to 3.4 Å. The columns are hexagonally packed with a first neighbour distance between columns which increases regularly from 27.6 to 35.2 Å in going from the C_6 to the C_{12} alkoxy derivative. Below the transition temperature the phthalocyanine moeities are still stacked but the individual Pc units are tilted with respect to the columnar axis and the average Pc to Pc, centre-to-centre distance is 4.2 Å.

These substances have been pulse-irradiated, as compressed powders, using nanosecond duration pulses of 3 MeV electrons from a Van de Graaff accelerator. Because of the low linear-energy-transfer (LET) of this type of radiation with a distance of greater than 1000 Å between energy deposition events along the track of a primary electron, the medium can be considered to be uniformly ionized. Since energy is deposited according to the electron density of the medium, ionization will occur initially in both the saturated hydrocarbon and phthalocyanine regions. Phthalocyanine units will however act as very efficient trapping sites for both electrons and holes formed in the intervening aliphatic hydrocarbon medium and these charge carriers would be expected to become very rapidly localised within the Pc cores of the stacks. Despite this rapid localisation, pulsed irradiation of these materials with alkyl chain lengths of 6, 9 and 12 carbon atoms is found to result in large and long-lived conductivity transients as is illustrated in figure 6. (For details of this type of TRMC measurement on microheterogeneous, powder samples consult references 1 and 3).

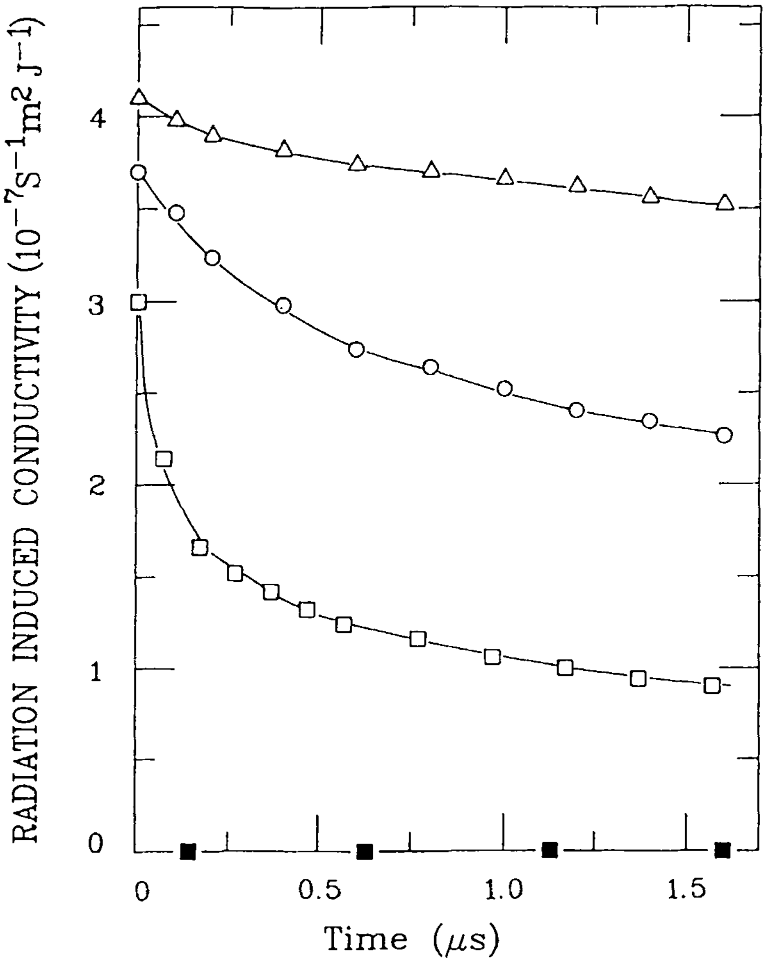

FIGURE 6 Microwave conductivity transients found on pulse-radiolysis (10 ns, 3 MeV electrons) of the compounds shown in figure 5 with n = 1, filled squares; 6, open squares; 9, open circles; and 12, open triangles.

A particularly interesting aspect of the results is that the timescale of the decay of the conductivity increases dramatically with increasing alkyl chain length, see table I; by approximately a factor of 10 for each increase by three carbon atoms.

TABLE I

CHARGE RECOMBINATION KINETICS IN PULSE-IRRADIATED OCTA-n-ALKOXYPHTHALOCYANINES

n	T_c^a (°C)	D_c^b (Å)	Recombination Half-Life (μs)		
			ca 20°C	$(T_c - 10)^a$	$(T_c + 10)^a$
6	115	27.6	0.30	0.80	1.95
7		28.8			
8		30.3			
9	104	31.4	3.0	5.8	17
10		32.6			
11		33.9			
12	90	35.2	35	70	250

[a] heating trajectory [b] intercolumnar distance in the mesophase at 200°C.

In addition we find that irradiation of the methyl derivative results in no measurable conductivity change.

We interpret the results in the following way: Ionisation occurs uniformly throughout the solid. Electrons and holes either undergo rapid geminate recombination or diffuse apart and become trapped within the cores of phthalocyanine stacks. The individual carriers are highly mobile along the axis of the cores and if oppositely charged carriers are present within a given stack they undergo rapid (subnanosecond) recombination. A fraction of the positive and negative carriers become trapped on separate stacks. Recombination of these carriers can now only occur via electron tunnelling through the surrounding hydrocarbon mantle which presents an insulating barrier. The lifetime of these carriers is therefore considerably increased and becomes sensitive to the thickness of the hydrocarbon mantle, i.e. the length of the alkyl chains. In the case of the methyl derivative it would appear that the barrier to recombination is negligible allowing it to take place on a subnanosecond timescale.

The kinetics of the decay of the conductivity transients in the long chain compounds is non-exponential indicating that the recombination occurs not just by tunnelling between nearest neighbour stacks but also from second nearest neighbours and further. We are at present attempting to mathematically model this process. In the absence of a theoretical model we take as a parameter characterising the timescale of the tunnelling process the first half-life of the decay. These values are given in table I for room temperature and for temperatures 10 degrees below and 10 degrees above the transition from the crystalline solid to the ordered columnar mesophase. From the values for the mesophase, for which the nearest neighbour distances are accurately known, we find the dependence of $t_{½}$ on distance to be exponential i.e.

$$t_{½}(R) = t_{½}(0)\exp(aR) \qquad (5)$$

with $t_{½}(0) = 1.4\times10^{-8}$ s and $a = 0.64$ Å^{-1}.

If the increase in distance with increasing alkyl chain length is taken to be closely similar in the solid phase to that in the mesophase then the exponential tunnelling parameter "a" is found to have a value very close to that in the mesophase. Clearly however from the data in table I, the absolute values for a given compound undergo a marked change at the transition temperature with the half-life in the solid being approximately a factor of three shorter. This could be due to a decrease in the coupling efficiency of the hydrocarbon barrier in the mesophase resulting from the partial "melting" of the hydrocarbon chains. However since the core-to-core distance is expected to decrease in the solid due to the tilting of the molecules in the stacks, this could also explain the increased rate of tunnelling. At present we tend to prefer the latter explanation.

CONCLUSION

From studies on systems with very well defined structural geometries, we have found that charge recombination occurs through saturated hydrocarbon barriers with a rate that is exponentially dependent on the barrier thickness. For intramolecular recombination in donor-acceptor molecules with norbornane-type bridges the exponential distance parameter is found to be 0.88 Å^{-1}. Since it is thought that the bridging unit may not be simply an "inert" spacer, it might be expected that this parameter would be dependent on the nature of the intervening hydrocarbon medium. Very pronounced effects on the rate of charge separation have in fact been found when the completely all-trans arrangement of the intervening norbornane skeleton is deliberately removed[12] by introducing s-cis elements.

Our value of 0.64 Å^{-1} for electron transfer through what are basically barriers consisting of outstreched *n*-alkyl chains would support this sensitivity of electron tunnelling to the nature of the intervening barrier. This parameter is however not significantly affected by "melting" of the chains and removal of the strict all-trans configuration which is known to occur at the transition from the crystalline solid to the mesophase of the phthalocyanine compounds studied. Even the absolute value of the rate does not appear to be significantly affected if the changes occurring concurrently in the core-to-core distance are taken into account.

Considerably larger values of "a" (*ca* 1.2 Å^{-1}) have been determined for electron transfer between randomly distributed sites in low temperature glassy matrices[13] and values as low as *ca* 0.3 Å^{-1} have been reported from fluorescence quenching results in Langmuir-Blodgett films[14]. In these studies however the actual distances involved were either very disperse or not accurately known.

An aspect of equal interest is the role of the bulk medium in the recombination kinetics. The results in the first section certainly indicate a dramatic effect of solvent on the absolute rate of recombination. The cause of this effect does not lie in a change in the exponential distance parameter however but rather in the preexponential frequency factor and it is almost certainly related to the magnitude and mode of dissipation of the excess energy evolved in the neutralisation process.

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REFERENCES

1) J.M. Warman and M.P. de Haas, "Pulse Radiolysis in Irradiated Systems", (CRC Press, in press) Y. Tabata ed.
2) M.P. de Haas and J.M. Warman, Chem. Phys.,73, 35 (1982).
3) J.M. Warman, M.P. de Haas and H.M. Wentinck, Radiat. Phys. Chem., in press.
4) M.N. Paddon-Row, A.M. Oliver, J.M. Warman, K.J. Smit, M.P. de Haas, H. Oevering and J.W. Verhoeven, J. Phys. Chem., 92, 6958 (1988).
5) D.C. Craig and M.N. Paddon-Row, Aust. J. Chem., in press.*****
6) J.M. Warman, M.P. de Haas, M.N. Paddon-Row, E. Cotsaris, N.S. Hush, H. Oevering and J.W. Verhoeven, Nature, 320, 615 (1986).
7) H. Oevering, M.N. Paddon-Row, M. Heppener, A.M. Oliver, E. Cotsaris, J.W. Verhoeven and N.S. Hush, J. Am. Chem. Soc., 109, 3258 (1987).
8) H. Oevering, J.W. Verhoeven, M.N. Paddon-Row and J.M. Warman, Tetrahedron, 45, 4751 (1989).
9) K.J. Smit, J.M. Warman, M.P. de Haas, M.N. Paddon-Row and A.M. Oliver, Chem. Phys. Lett., 152, 177 (1988).
10) R.A. Marcus, J. Chem. Phys., 24, 966 (1956).
11) R.A. Marcus and N. Sutin, Biochim. Biophys. Acta.,811, 265 (1985).
12) A.M. Oliver, D.C. Craig, M.N. Paddon-Row, J. Kroon and J.W. Verhoeven, Chem. Phys. Lett., 150, 366 (1988)
13) J.R. Miller, J.V. Beitz and R.K. Huddleston, J. Am. Chem. Soc., 106, 5057 (1984)
14) H. Kuhn, J. Photochem., 10, 111 (1979).
15) J.F. van der Pol, E. Neeleman, J.W. Zwikker, R.J.M. Nolte and W. Drenth, Rec. Trav. Chim. Pays-Bas, 107, 615 (1988).
16) J.F. van der Pol, E. Neeleman, J.W. Zwikker, R.J.M. Nolte, W. Drenth, J. Aerts, R. Visser and S.J. Picken, Liq. Cryst., in press.