

Photo-induced electron transfer in polychromophoric systems

M. Van der Auweraer, F.C. De Schryver, G. Verbeek, A. Vaes, N. Helsen, P. Van Haver, S. Depaemelaere

Laboratory for Molecular Dynamics and Spectroscopy K.U.Leuven Celestijnenlaan 200-F, B-3001 Heverlee, Belgium.

D. Terrell, S. De Meutter

Agfa-Gevaert N.V. Septestraat 27, B-2650 Mortsel, Belgium.

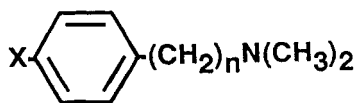
Abstract

Combining stationary and time resolved fluorescence spectroscopy with laser-induced opto-acoustic spectroscopy allowed to investigate the influence of molecular structure and solvent polarity on the rate of the radiative and radiationless decay processes of exciplexes of ω -phenyl- α -N,N-dimethylaminoalkanes. By making intersystem crossing to the locally excited state less exergonic increasing the solvent polarity decreased the rate constant for intersystem crossing. The apparent decrease of the fluorescence rate constant in highly polar solvents was attributed to the direct formation of a solvent separated ion-pair. The formation of solvent separated ion-pairs can also explain why, contradicting the predictions of Marcus theory, the rate constant for internal conversion decreases sometimes in highly polar solvents. The solvent dependence of the fluorescence spectra of dialkylamino and diarylamino substituted triphenylbenzene derivatives indicates that in those completely symmetric molecules the emission occurs from a highly polar excited state. The exponential fluorescence decays suggest that equilibration between the different excited species occurs within the time resolution of the experimental set-up. The comparison of compounds with meta- and para-substitution and the comparison of dialkylamino and diarylamino derivatives suggests that either a conjugated intramolecular charge transfer state or a TICT state, in which the amino or the anilino moiety rotates out of the plane of the triphenylbenzene moiety, are formed. Comparing the room temperature emission spectra with those at 77 K in isopentane glass allowed to obtain information on the geometry of the species emitting in less polar solvents.

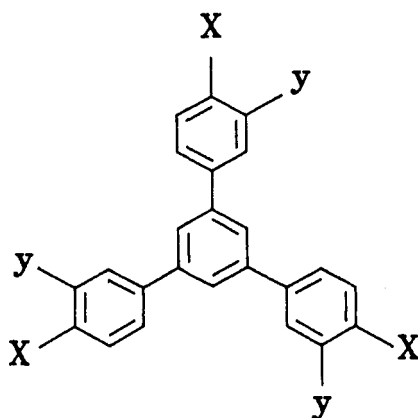
INTRODUCTION

The influence of the solvent polarity on the radiationless decay of intramolecular exciplexes between pyrene or naphthalene and electron donors (ref. 1) has already been investigated, using opto-acoustic spectroscopy and transient absorption spectroscopy. Upon investigation of the temperature dependence of the rate constant for radiationless decay of the exciplexes of ω -phenyl- α -N,N-dimethylaminoalkanes, **1**, **2**, **3**, determined using stationary and time resolved fluorescence spectroscopy, small values were obtained for the preexponential factor (10^7 to 10^9 s⁻¹) and the activation energy (0.5 to 5 kJ/mol) of this process (ref. 2-4). This suggested that the radiationless decay occurred mainly by intersystem crossing. Since the absorption coefficient of the triplet of toluene is very small at wavelengths above 300 nm (ref. 5) it is not possible to study the radiationless decay processes of the intramolecular exciplexes of the ω -phenyl- α -N,N-dimethyl amino alkanes using transient absorption spectroscopy. It remains however possible to investigate the radiationless decay of the exciplexes of ω -phenyl- α -N,N-dimethylaminoalkanes using laser induced opto-acoustic spectroscopy (LIOAS) (ref. 6-8).

For compounds in which a benzene ring forms the link between electron donor and electron acceptor moieties conjugated planar (ref. 9-10) structures as well as TICT states, in which the donor moiety rotates out of the plane of the acceptor (ref. 11-12), have been proposed. Later experiments suggested that TICT-formation is not limited to phenyl groups substituted in 1- and 4-position by strong electron donors and acceptors but that it occurs even in completely symmetrical molecules e.g. bianthryl (ref. 13-16) and others (ref. 17). While up to now most of the examples of symmetry breaking after excitation are characterized by the presence of condensed polycyclic hydrocarbons and a twofold symmetry, in the present contribution an example with threefold symmetry, **4**, **5** and **6**, resembling to some extent the triphenylphosphines discussed by Rettig (ref. 18), in which a polyphenylene moiety acts as the acceptor group, will be discussed.



<u>1</u>	n = 2	X = H
<u>2</u>	n = 2	X = CN
<u>3</u>	n = 3	X = H



<u>4</u>	X = NR ₂	Y = H	R =
<u>5</u>	X = H	Y = NR ₂	R =
<u>6</u>	X = H	Y = NR ₂	R = C ₂ H ₅

For [4-[bis(4-ethylphenyl)amino]phenyl]-N,N,N',N',-tetrakis(4-ethylphenyl)-[1,1':3',1"-terphenyl]-4,4"diamine, 4, (p-EFTP) and 5'-[3-[bis(4-ethylphenyl)amino]phenyl]-N,N,N',N',-tetrakis(4-ethylphenyl)-[1,1':3',1"-terphenyl]-3,3"diamine, 5, (m-EFTP) the emission in polar solvents (ref. 19)) is due to a species with a dipole moment of respectively 26.7 ± 1.5 and 31.8 Debye. Although in less polar solvents the emission is due to a species with a smaller excited state dipole moment there is up to now no experimental evidence suggesting dual emission. While the species emitting in less polar solvents is a conjugated intramolecular (ref. 20-25) charge transfer state the dipole moments of the species emitting in polar solvents are compatible with a state where a diphenylamino or a triphenylamino moiety, acting as an electron donor, is decoupled from the rest of the molecule as is e.g. the case in a TICT state. Recent results suggest however a similar photophysical behaviour in molecules where the donor group cannot reach an orientation perpendicular to the acceptor group (ref. 26). On the other hand 5'-[3-[diethylamino]phenyl]-N,N,N',N',-tetrakisethyl-[1,1':3',1"-terphenyl]-3,3"diamine, 6, (m-ETP) is characterized by an excited state dipole moment of 15.2 Debye which does not depend upon the solvent polarity. This suggests that in all solvents symmetry breaking leads to a conjugated intramolecular charge transfer state in 6. In order to obtain more information on the nature and conformation of the excited state of the species emitting in apolar solvents the emission and excitation spectra of 4, 5 and 6 were obtained in isopentane glass at 77 K.

EXPERIMENTAL

The preparation and purification of the ω -phenyl- α -N,N-dimethylaminoalkanes, 2-phenyl-N,N-dimethylaminoethane, 1 (P2NM), 3-phenyl-N,N-dimethylaminopropane, 2 (P3NM) and 2-(4-cyanophenyl)-N,N-dimethylaminoethane, 3 (PCN2NM) and the amino-substituted triphenylbenzenes, 4, 5 and 6, have been reported earlier (ref. 27-28). All solvents were of spectroscopic or fluorescence grade and were used as received. All solutions used for stationary and time-resolved fluorescence measurements were degassed by freeze-pump-thaw cycles. Absorption spectra were recorded with a Perkin Elmer Lambda 6 UV/VIS spectrometer. Corrected fluorescence and excitation spectra were obtained with a SPEX Fluorolog 212. The experimental set-up for the laser induced opto-acoustic spectroscopy (LIOAS) is described in detail elsewhere (ref. 1,8). The absorbance of the sample solutions used in the LIOAS experiments was always below 0.1 and the samples were degassed by bubbling argon for 15 min.

RESULTS AND DISCUSSION

Laser induced opto-acoustic spectroscopy (LIOAS) of *o*-phenyl-N,N-dimethyl amino alkanes

In the LIOAS experiments the fraction, α , of the absorbed laser energy, E_{abs} , that is converted into heat within the time constant of the experimental set-up (ref. 6-8), E_{th} , is determined. The mechanistic and thermodynamic scheme (ref. 1) that is used for the interpretation of the laser induced opto-acoustic experiments is shown in Fig. 1. In Fig. 1 k_{icm} and k_{iscm} indicate the rate constant of respectively internal conversion and intersystem crossing from the relaxed locally excited state S_{1m} ; k_{fm} is the rate constant of fluorescence from the locally excited state S_{1m} ; k_{ice} , k_{isce} and k_{fc} indicate the rate constant of respectively internal conversion, intersystem crossing and fluorescence from the exciplex; ΔH is the stabilisation energy of the exciplex and E_{rep} is the energy content of the Franck-Condon ground state reached after the exciplex decay. Combining the experimentally determined value of α (Table 1) with fluorescence quantum yields of the locally excited state (ref. 2-4,27), the exciplex and a model compound containing only the acceptor chromophore allows to determine β (Table 1), the fraction of the radiationless decay of the exciplex that occurs by internal conversion.

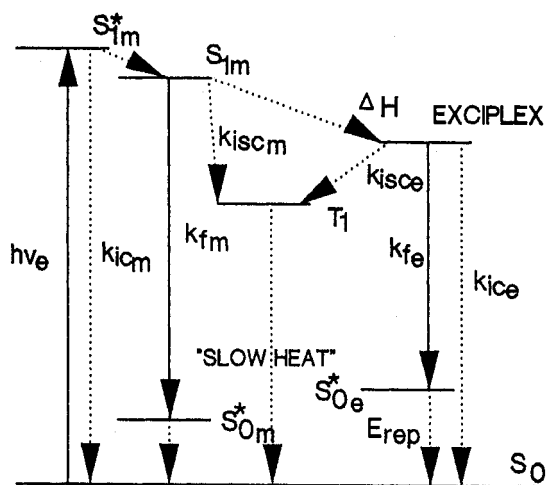


Fig. 1. Kinetic and thermodynamic scheme of the photo-physics of the bichromophoric compounds.

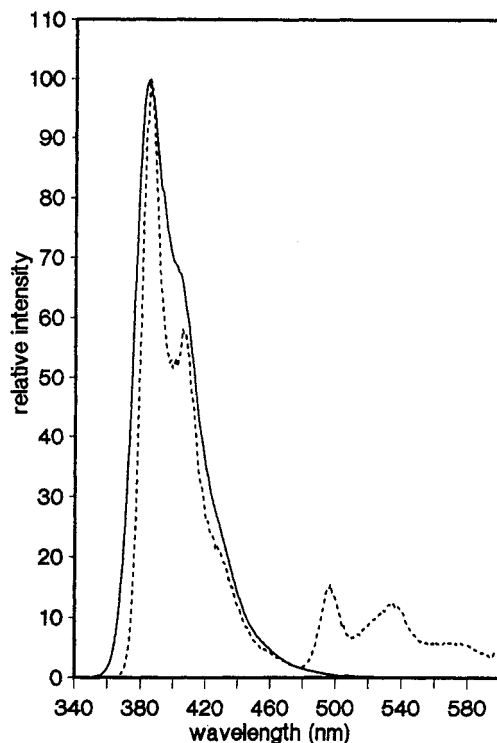


Fig. 2. Normalized emission spectra of **4** at room temperature in isoctane (—) and at 77 K in isopentane glass (.....).

$$\beta = k_{ice} / (k_{ice} + k_{isce}) \quad (1)$$

TABLE 1. Experimentally obtained values of α and β for **1**, **2**, and **3** in solvents of the different polarity.

	1		2		3	
	α	β	α	β	α	β
isoctane	0.65 ± 0.03	0.71 ± 0.05	0.50 ± 0.03	0.49 ± 0.04	0.65 ± 0.03	0.66 ± 0.05
tetrahydrofuran	0.81 ± 0.04	0.97 ± 0.08	0.65 ± 0.03	0.64 ± 0.05	0.80 ± 0.04	0.79 ± 0.06
acetonitrile	0.99 ± 0.05	1.02 ± 0.07	0.77 ± 0.04	0.71 ± 0.05	0.94 ± 0.05	0.93 ± 0.06

Combining the data given in Table 1 with the total rate constant of the exciplex decay (ref. 2-4, 27) and the exciplex fluorescence quantum yield allows to obtain the individual rate constants k_{ice} , k_{isce} and k_{fe} (Table 2). Table 1 and 2 suggest that α and β increase upon the solvent polarity. The increase of β suggests that increasing the solvent polarity favours internal conversion compared to intersystem crossing. These results can be rationalised in the framework of the current electron transfer theory (ref. 29-30). For all compounds investigated the intersystem crossing from the exciplex to the locally excited triplet state is characterized by values of ΔG° situated in the "normal" Marcus region or near the top of the Marcus parabola. Increasing the solvent polarity will make this process less exergonic and therefore either affect k_{isce} very little or even decrease k_{isce} . k_{ice} corresponds always to values of ΔG° situated very deeply in the inverted region and therefore increasing the solvent polarity, which makes this process less exergonic will enhance k_{ice} to a large extent. The increase of the reorganisation energy upon increasing the solvent polarity will enhance those effects. Combining the data of Table 1 and 2 with the earlier observed (ref. 2-5) temperature dependence of the radiationless decay suggests that the strongly exergonic internal conversion process leads to the population of a highly vibrationally excited ground state characterised by a small Franck-Condon factor (ref. 31-32). To explain the changes between tetrahydrofuran and acetonitrile of the apparent values of k_{ice} and k_{isce} observed for **3** the branching between an exciplex and a solvent separated ion pair has to be considered (ref. 33).

TABLE 2. Calculated values for the rate constants of intersystem crossing and internal conversion of the exciplex decay.

	k_{ice}	k_{iscc}	k_{fc}
<u>1</u> (isooctane)	$4.3 \times 10^7 \text{ s}^{-1}$	$1.8 \times 10^7 \text{ s}^{-1}$	$1.4 \times 10^7 \text{ s}^{-1}$
<u>1</u> (tetrahydrofuran)	$8.1 \times 10^7 \text{ s}^{-1}$	$2.5 \times 10^6 \text{ s}^{-1}$	$2.6 \times 10^7 \text{ s}^{-1}$
<u>1</u> (acetonitrile)	$2.4 \times 10^8 \text{ s}^{-1}$	$< 1.0 \times 10^7 \text{ s}^{-1}$	$1.0 \times 10^7 \text{ s}^{-1}$
<u>2</u> (isooctane)	$2.5 \times 10^7 \text{ s}^{-1}$	$2.6 \times 10^7 \text{ s}^{-1}$	$1.7 \times 10^7 \text{ s}^{-1}$
<u>2</u> (tetrahydrofuran)	$3.1 \times 10^7 \text{ s}^{-1}$	$1.7 \times 10^7 \text{ s}^{-1}$	$9.8 \times 10^6 \text{ s}^{-1}$
<u>2</u> (acetonitrile)	----- (a)	----- (a)	----- (a)
<u>3</u> (isooctane)	$7.7 \times 10^7 \text{ s}^{-1}$	$3.9 \times 10^7 \text{ s}^{-1}$	$2.7 \times 10^7 \text{ s}^{-1}$
<u>3</u> (tetrahydrofuran)	$3.4 \times 10^7 \text{ s}^{-1}$	$9.0 \times 10^6 \text{ s}^{-1}$	$9.9 \times 10^6 \text{ s}^{-1}$
<u>3</u> (acetonitrile)	----- (a)	----- (a)	----- (a)

(a) exciplex emission too weak to determine decay times.

Symmetry breaking in the excited state of triphenylbenzenes

In isopentane at 77 K, where it can be expected that no large amplitude motions involving e.g. the rotation of a diphenylamino or a triphenylamino moiety are possible within the excited state decay time, the fluorescence spectrum of 4 (Fig. 2) consists of a maximum at 385 nm (0-0 transition), a secondary maximum at 405 nm (0-1 transition) and a shoulder at 425 nm (0-2 transition). On the other hand a room temperature, where rotation of a bulky group is possible within the excited state decay time, the emission maximum is situated at 384 nm with a shoulder at 400 nm. This suggests that along the coordinates involving a large amplitude vibration (rotation of a diphenylamino or a triphenylamino moiety, hybridization of the nitrogen) no important shift of the potential energy minimum occurs upon excitation. The large Stokes shift in apolar solvents (from 341 nm to 385 nm) is therefore not due to a different position of the energy minima of the ground state and the first singlet excited state. This suggests that the absorption band of the first excited state is hidden below the long wavelength tail of the band with a maximum at 341 nm. This allows to explain why the experimentally observed value of the fluorescence rate constant of 4 in isooctane is three times lower than that calculated using the Strickler Berg equation (ref. 34-35). Beside the fluorescence spectrum with a maximum at 385 nm the emission spectrum in isopentane glass at 77 K shows a second transition with maxima at 497 nm and 534 nm and a shoulder at 572 nm. This band can be attributed to phosphorescence of 4. This suggests that the triplet of 4 is situated at 20120 cm^{-1} in isopentane glass at 77 K. If the triplet energy of 4 does not depend upon the solvent polarity intersystem crossing from the singlet state to the triplet state will become less exergonic upon increasing the solvent polarity. This could explain why the rate constant for the nonradiative decay of 4 decreases from $7.2 \times 10^8 \text{ s}^{-1}$ in isooctane to $4.3 \times 10^8 \text{ s}^{-1}$ in acetonitrile.

Also for 5 the fluorescence spectrum at 77 K in isopentane (Fig. 3) is characterized by a maximum at 395 nm and a secondary maximum at 403 nm (0-1 transition). As the maximum of the emission spectrum is situated at 393 nm at room temperature the argumentation developed for 4 suggests that also for 5 the equilibrium conformation does not change upon excitation in apolar solvents. Similar results have been obtained for triphenylamine in molecular beams and clusters of triphenylamine and argon (ref. 36). Also for 5 the large Stokes shift observed in apolar solvents (from 298 to 393 nm) is rather due to the presence of transition hidden under the tail of the band with a maximum at 298 nm than to an important relaxation of the molecular geometry after excitation. Also in this case the discrepancy between the experimentally observed fluorescence rate constant in isooctane ($7.8 \times 10^8 \text{ s}^{-1}$) and that calculated using the Strickler Berg (ref. 34-35) equation ($8.7 \times 10^8 \text{ s}^{-1}$) is due the fact the absorption band with a maximum at 298 nm is not due to the transition between the ground state and the first singlet excited state. The solvent dependence of the emission maximum in solvents with a polarity varying from isooctane to diethylether suggests the formation of a conjugated intramolecular charge transfer state. Beside the fluorescence spectrum with a maximum at 395 nm the emission spectrum in isopentane glass at 77 K shows a second transition with maxima at 460 nm and 487 nm and shoulders at 524 nm and 558 nm. This band can be attributed to phosphorescence of 5. This suggests that the triplet of 5 is situated at 21740 cm^{-1} in isopentane glass at 77 K. Using the argumentation developed for 4, the decrease of the rate constant for the nonradiative decay of 5 from $2.9 \times 10^8 \text{ s}^{-1}$ in isooctane to $1.1 \times 10^8 \text{ s}^{-1}$ in acetonitrile could be explained by a decrease of the rate constant for intersystem crossing in polar solvents. The smaller relative intensity of the phosphorescence of 4 is probably due to the considerably smaller quantum yield for the radiationless decay (intersystem crossing) of the singlet state.

The fluorescence spectrum of 6 in isopentane glass at 77 K (Fig. 4) consists of a band with maxima at 362 nm (0-0 transition) and at 375 nm (0-1 transition). This corresponds to a hypsochromic shift over 1140 cm^{-1} compared to the emission maximum at room temperature in isooctane. The hypsochromic shift, due to blocking of the large amplitude motions, suggests that upon excitation an important shift of the minimum occurs along one of those coordinates. As the excited state of 6 is a conjugated intramolecular charge transfer state in solvents with a polarity ranging from that of isopentane to that of acetonitrile this conformational relaxation from the Franck Condon excited state is probably linked to an increased coplanarity of the phenyl moieties (ref. 37-38) or an increased p-character of the nitrogen lone pairs.

In the ground state the π -bond order between the central phenyl moiety and the peripheral phenyl moieties amounts to 0.368. As in the framework of the Hückel MO-theory the HOMO and the LUMO of 6 in a planar conformation, or a conformation where the three diethylanilino moieties are twisted over the same angle, are doubly degenerate it is however not possible to obtain the order of the π -bonds between the central phenyl moiety and the peripheral diethylanilino moieties in the first excited state. However as the Hückel calculations suggest that in several excited state configurations the double bond character of the bond between the central phenyl ring and the peripheral diethylanilino moieties is always increased the equilibrium conformation of the excited state can be expected to be more coplanar than that of the ground state. This excited state can become polarized by a suitable configuration interaction between the four configurations that are isoenergetic in the framework of the Hückel MO theory. The large Stokes shift in isopentane at 77 K (from 332 to 362 nm) suggests the absorption band with a maximum at 332 nm is not due to a transition to the first excited singlet state. This could explain why the fluorescence rate constant calculated using the Strickler Berg equation is five times larger than the experimentally observed fluorescence rate constant.

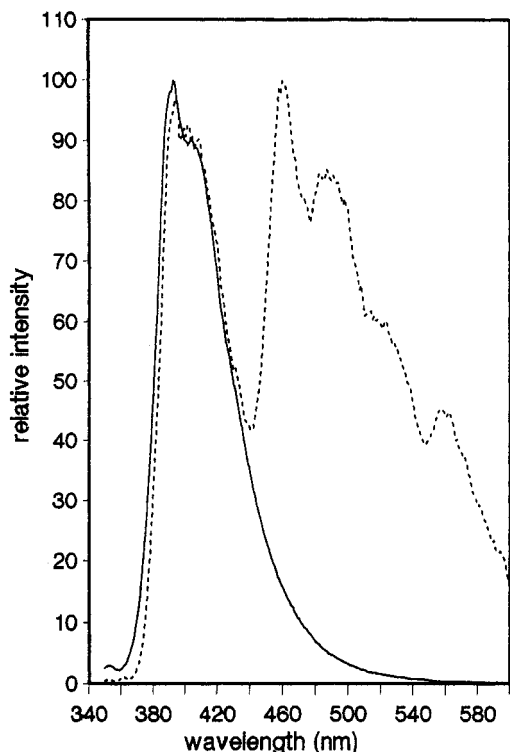


Fig. 3. Normalized emission spectra of 5 at room temperature in isooctane (—) and at 77 K in isopentane glass (.....).

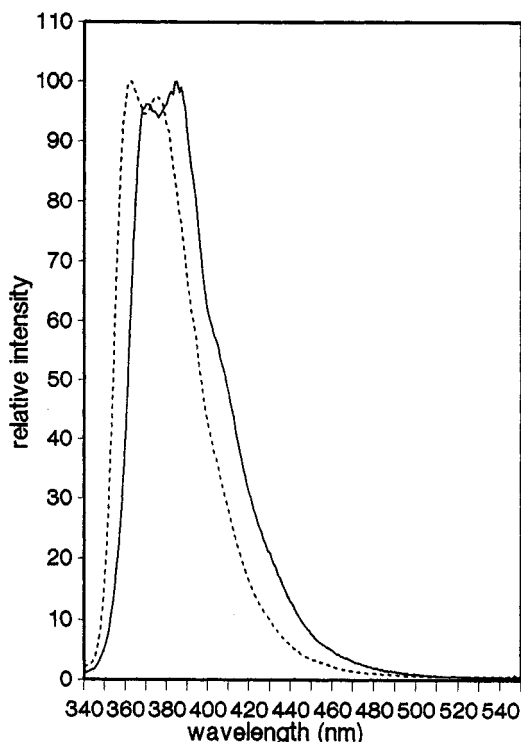


Fig. 4. Normalized emission spectra of 6 at room temperature in isooctane (—) and at 77 K in isopentane glass (.....).

While the experimental results allow to obtain information on the excited state of 4 and 5 in less polar solvents and on that of 6 in all solvents the situation is more complicated for 4 and 5 in strongly polar solvents. For those molecules the formation of a TICT state cannot be excluded. In this TICT state either the diphenylamino or the a triphenylamino moiety acting as electron donor could be twisted. When a triphenylamino group is rotated a dipole moment of respectively 36.3 and 32.5 Debye would be expected for 4 and 5 respectively. If a diphenylamino group would be twisted the dipole moment would amount to 26.7 and 23.3 Debye respectively. Correlating the emission energy with the Coulomb (ref. 39-41) interaction between the positive and the negative excess charge in both parts of the molecule excludes that both molecules form a TICT state where a triphenylamino moiety is twisted. This argument is supported by the fact that in this case the excited state dipole moment of 4 should be 15 % larger than that of 5 while the experimental results suggest that the excited state dipole moment of 4 is in polar solvents 15 % smaller than that of 5. For the slopes of the Lippert-Mataga plots (ref. 42-43) the discrepancy should be even a larger. If both 4 and 5 would form a TICT state in polar solvents the relative values of both excited state dipole moments suggest that while in 4 a diphenylamino moiety is twisted while in 5 a triphenylamino moiety is twisted. It can however not be excluded that in one or both molecules a conjugated intramolecular charge transfer state is formed in polar solvents.

The experimental results suggest that symmetry breaking leading to a polar excited should not automatically suggest the formation of a TICT state. The nature of the polar species formed will depend upon the energy of the locally excited

states relative to that of the charge transfer state (ref. 39,44) as well as on the presence of steric interactions. A further elucidation of the nature of the excited state would require the determination of the fluorescence decays (ref. 10, 26) with a larger time resolution and the wavelength dependence of the fluorescence polarisation.

Acknowledgements

M.V.D.A. is a "Onderzoeksleider" of the Belgian "Fonds voor Kollektief Fundamenteel Onderzoek". The authors thank Agfa-Gevaert N.V. for financial support and a scholarship to G.V.. The continuing support of the Belgian "Fonds voor Kollektief Fundamenteel Onderzoek" and the Ministry of Science Programming through IUAP 16 and IUAP-040 is gratefully acknowledged.

REFERENCES

1. Ph. Van Haver, N Helsen, S. Depaemelaere, M. Van der Auweraer and F.C. De Schryver *J. Am. Chem. Soc.* **113**, 6849-6857 (1991).
2. M. Van der Auweraer, A. Gilbert and F.C. De Schryver *J. Am. Chem. Soc.* **102**, 4007-4017 (1980).
3. M Van der Auweraer, A. Gilbert and F.C. De Schryver. *J. Phys. Chem.* **85**, 3198-3205 (1981).
4. M. Van der Auweraer, A. Vannerum and F.C. De Schryver *J. Mol. Struct.* **84**, 343 (1983).
5. F. Wilkinson In *Org. Molecular Photophysics*, Vol 2, p. 217, J.B. Birks, Ed., Wiley, London (1975).
6. C.K.N. Patel and A.C. Tam *Appl. Phys. Lett.* **34**, 467-470 (1979).
7. K. Heihoff and S. Braslavsky *Chem. Phys. Lett.* **131**, 183-188 (1986).
8. Ph. Van Haver, M. Van der Auweraer and F.C. De Schryver *J. Photochem. Photobiol. A:Chem.* **63**, 265-277 (1992).
9. H.K. Sinha and K. Yates *J. Am. Chem. Soc.* **113**, 6062-6067 (1991).
10. T.P. Carsey, G.L. Findley and S.P. Mc Glynn, *J. Am. Chem. Soc.* **101**, 4502-4517 (1979).
11. W. Rettig and V. Bonačić-Koutecký *Chem. Phys. Lett.* **62**, 115-120 (1979).
12. Z.R. Grabowski, K. Rotkiewicz, A. Siemiarczuk, D. Cowley and J.W. Baumann *Nouveau Journal de Chimie* **3**, 443-454 (1979).
13. F. Schneider and E. Lippert *Ber. Bunsenges. Phys. Chem.* **74**, 624-630 (1970).
14. W. Rettig and M. Zander, *Ber. Bunsenges. Phys. Chem.* **87**, 1143-1149 (1983).
15. N. Mataga, H. Yao, T. Okada and W. Rettig *J. Phys. Chem.* **93**, 3383-3386 (1989).
16. P.F. Barbara and W. Jarzaba *Advan. Photochem.* **15**, 1-137 (1990).
17. W. Rettig *Angewandte Chemie Int. Ed. Engl.* **25**, 971-988 (1986).
18. M. Vogel, W. Rettig and P. Heimbach *J. Photochem. Photobiol. A* **61**, 65-75 (1991).
19. G. Verbeek, S. Depaemelaere, M. Van der Auweraer, F.C. De Schryver, A. Vaes, D. Terrell, S. De Meutter submitted.
20. L.G.S. Brooker, G.H. Keyes and D.W. Heseltine *J. Am. Chem. Soc.* **73**, 5350-5356 (1951).
21. L.G.S. Brooker, A.C. Craig, D.W. Heseltine, P.W. Jenkins and L.L. Lincoln *J. Am. Chem. Soc.* **87**, 2443-2450 (1965).
22. H.G. Benson and J.N. Murrell, *J. Chem. Soc. Faraday Transactions II* **68**, 137-143 (1972).
23. Th. Förster *Z. Elektrochem.* **45**, 549-573 (1939).
24. M.J. Kamlet, J.-L. Abboud and R.W. Taft *J. Am. Chem. Soc.* **99**, 6027-6038 (1977).
25. W.T. Simpson, *J. Am. Chem. Soc.* **73**, 5359-5363 (1951).
26. U. Leinhos, W. Kühnle and K. Zacchariasse, *J. Phys. Chem.* **95**, 2013-2021 (1991).
27. Ph. Van Haver, L. Viaene, M. Van der Auweraer, F.C. De Schryver, in preparation.
28. M. Van Der Auweraer, F.C. De Schryver, G. Verbeek, C. Geelen, D. Terrell, and S. De Meutter *Eur. pat. EP* 349034
29. P. Siders and R. Marcus, *J. Am. Chem. Soc.* **103**, 741-747 (1981).
30. R. Marcus, *J. Chem. Phys.* **81**, 4494-4500 (1984).
31. S. Efrima and M. Bixon, *Chem. Phys. Lett.* **25**, 34-37 (1974).
32. J. Jortner and M. Bixon *J. Chem. Phys.* **88**, 167-170 (1988).
33. H. Knibbe, K. Röllig, F. Schäfer and A. Weller *J. Chem. Phys.* **47**, 1184-1185 (1967).
34. S.J. Strickler and R.A. Berg *J. Chem. Phys.* **37**, 814-822 (1962).
35. J.B. Birks, D.J. Dyson *Proc. Roy. Soc. A* **275**, 135-148 (1963).
36. G. Meijer, G. Berden, W.L. Meerts, H. Hunziker, M. S. de Vries and H.R. Wendt, *Chem. Phys.* **163**, 209-222 (1992).
37. H. Jaffé, and M. Orchin *Theory and Applications of Ultraviolet Spectroscopy*, Wiley, New York (1962).
38. J.N. Murrell *The Theory of Electronic Spectra of Organic Molecules*, Wiley, New York, (1963).
39. M. Van der Auweraer, Z.R. Grabowski and W. Rettig *J. Phys. Chem.* **95**, 2083-2092 (1991).
40. A.M. Swinnen, M. Van der Auweraer, F.C. De Schryver *J. Photochemistry* **28**, 315-328 (1985).
41. A.M. Swinnen, M. Van der Auweraer, F.C. De Schryver, K. Nakatani, T. Okada, N. Mataga *J. Am. Chem. Soc.* **109**, 321-330 (1987).
42. N. Mataga, Y. Kaifu, M. Koizumi, *Bull. Chem. Soc. Jpn.* **28**, 690-691 (1955).
43. E. Lippert *Z. Naturf.* **10a**, 541-545 (1955).
44. E. Lippert, W. Rettig, V. Bonačić-Koutecký, F. Heisel and J.A. Miehé *Adv. Phys. Chem.* **68**, 1-173 (1987).