

Electron transfer in flexible molecules and molecular ions

Zbigniew R. Grabowski

Institute of Physical Chemistry, Polish Academy of Sciences
Kasprzaka 44, 01-224 Warsaw, Poland

Abstract. Electron transfer (ET) occurring in or after electronic excitation in flexibly bonded donor-acceptor (D-A) molecules are accompanied by structural relaxation. In singly bonded D-A molecules often the "twisted" intramolecular charge transfer (TICT) structures are formed. Evidence for the TICT hypothesis is presented. In some compounds behaviour deviating from the original TICT model is observed; strict applicability of that hypothesis seems to be limited to rather simple D-A molecules. Most deactivation processes involve back ET. Kinetic data on the fluorescence rise and decay seem not always to correspond to the real population kinetics in the case of forbidden transitions in emission; a hot luminescence emitted along the reaction path may distort the curves at short delay times. Contrary to neutral D-A molecules, photophysics of ET in the molecular ions, $D-A^+$, are much less understood: most often, unexpectedly fast radiationless processes (back ET ?) quench the emission.

PHOTOINDUCED ELECTRON TRANSFER AND THE STRUCTURAL RELAXATION

Electron transfer (ET) in the excited state, limited in the present paper to the intramolecular case, is accompanied or followed by relaxation of the neighbouring solvent [1,2], and of the molecular structure of the solute itself [3]. Jabłoński described a supramolecular system: excited solute + its solvent environment, as a "luminescent centre" [4]; usually the relaxation of the luminescent centre as a whole is observed. Under selected conditions (temporal resolution; inert nonpolar solvent; gas phase; rigid molecular structure of the solute) one can recognize the features of each contribution.

Solvent relaxation is similar to the other ET processes [5], except for specific excited state interactions, e.g., hydrogen bonding at specific positions [6], or those leading to solute-solvent exciplexes [7].

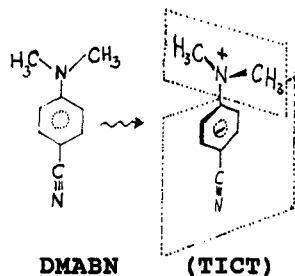
If the ET occurs between a donor (D^Z) and acceptor (A^Y) subsystems of the solute molecule ($D--A$)^{Z+Y} (where "--" denotes any type of intramolecular bridge), the relaxation of the solute structure, on the excited state level, ends in an intramolecular charge-transfer (ICT) excited state. This structural relaxation in the reaction: $(D^Z--A^Y)^* \rightarrow (D^{Z+1}--A^{Y-1})^*$ can be described as determined by three main factors:

(i) adaptation of the molecular structures of the original subsystems, D^Z and A^Y , to those resulting from the ET, i.e., resembling the free radicals or radical ions D^{Z+1} and A^{Y-1} . As an example a simple aliphatic amine can be shown, where NR_3 is pyramidal, while NR_3^+ flat and trigonal; it seems to be similar in ICT states with $-NR_2$ as the donor [8,9];

(ii) interaction of two moieties, D^{z+1} and A^{y-1} , specially pronounced in neutral molecules ($z=y=0$) where the ET leads to a separation of charges; radical ions of opposite charge, D^+ and A^- , appearing as sub-systems in the ICT state, mutually attract by coulombic force (so-called "harpooning effect" [10]). In flexible or semi-flexible molecules this can bring them close together, as in the intramolecular sandwich exciplexes formed from polymethylene-chain-linked D--A molecules [11], or in the remarkable case of a chair-to-boat conversion of the piperidine ring on ET [12,13]. Along with a coulombic interaction, the conformation of an ICT state is determined by both, stabilizing and destabilizing interactions - with higher excited states, and with the ground state, respectively [14];

(iii) interactions with the solvent. Both, the specific interactions mentioned above, and the general (non-specific) interactions with the polar and/or polarizable medium, differentiate the excited states: the ICT states are preferentially stabilized in polar solvents [15], the $n\pi^*$ states are destabilized in protic solvents [16], etc. As a result, the interactions between the electronic states change, affecting the ICT state conformation (e.g., the "proximity effects" [17]).

In flexible molecules the structure of an ICT state depends on all these factors. Cognition of the structure is usually easier for the theory than for the experiment [18,19,3]. Much evidence is gained by using appropriate model compounds with some conformations fixed - or excluded - for structural reasons.



Specially interesting are the cases with limited flexibility, represented by singly bonded D-A molecules; roughly, they have only one internal degree of freedom for conformational change: that of internal rotation.

D-A MOLECULES AND THE T.I.C.T. STATES

TICT hypothesis and proof

Discovery by Lippert et al. [15] of the dual fluorescence of 4-N,N-dimethylamino-benzonitrile (DMABN) stimulated a long controversy on the origin of the phenomenon. DMABN exhibits two fluorescence bands, whereby one is a "normal" band (often denoted as "b"), while the long-wave band ("a") appears only in polar solvents, growing with the polarity and shifting strongly to the red. Rotkiewicz et al. [8], basing on anisotropy of transitions and on steric effects of substituents, suggested the a band to correspond to the 90° twisted rotamer, for which sometime later the term "twisted ICT excited state" (TICT) has been coined [20,21], and is widely in use [22]. This general term was introduced when it became evident that it fits not only to DMABN, but to a variety of different D-A molecules as well.

The excited state dipole moments well correspond to the full charge transfer from the centre of D to the centre of A [23]; the thermodynamic [24] or quantum chemical calculations [25] fit to the observed data; also the steric effects give a strong evidence for the 90° twist of D vs. A.

The best evidence comes from comparison of several series of rather simple compounds. If some energetic and kinetic conditions [9,24] are fulfilled, only the derivatives with a rotatable dialkylamino group exhibit two fluorescence bands in moderately polar solvents. Those with an amino group immobilized in a 5-membered ring and conjugated with the aromatic system, emit the primary fluorescence b only; those with the amino group deviating

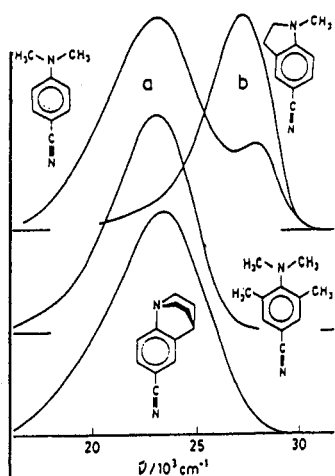


Fig.1. Emission spectra in CH_2Cl_2 of model compounds for DMABN [9].

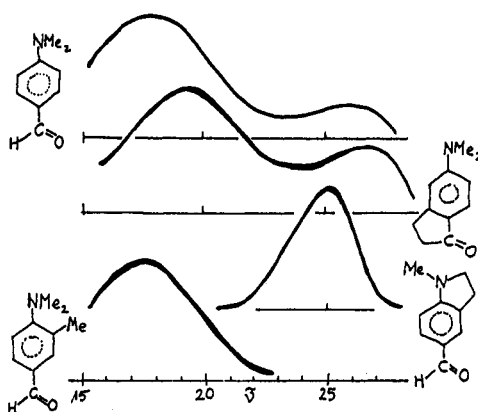


Fig.2. Fluorescence spectra of several *p*-carbonyl derivatives of dialkylaniline in CH_3CN (after [26,27]).

much from coplanarity with the aromatic system - by a steric effect of substituent, or in a rigid cage amine structure (Fig.1) - are characterized by a single emission band **a** only, from a highly polar emitting state, independent of the solvent.

The examples belong to the 4-dialkylamino-derivatives of benzonitrile (Fig.1), of benzaldehyde (Fig.2), and of pyrimidine (Fig.3). In the case of 4-dimethylamino-benzaldehyde quantum chemical calculation made equally probable two highly polar structures: this with the $-\text{NMe}_2$, or that with the $-\text{CHO}$ rotated by 90° ; the experiment with suitable model compounds (Fig.2) gave an unmistakable answer that the first alternative is true [26].

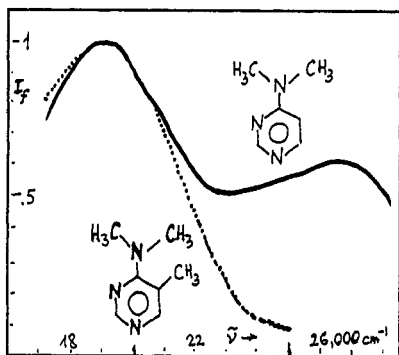


Fig.3. Emission of 4- NMe_2 -pyrimidines in CH_3OH [32].

Very pronounced steric effect appears also in the luminescence of these compounds in the supersonic molecular jets (Fig.4). One ortho methyl group is needed to find a red shifted band on excitation of a Van der Waals cluster of the molecule with 1 or 2 polar molecules [28]. In the strongly sterically hindered molecules (with two *o*-methyl groups), both in the gas [22,29] and in the jet [30], only the red shifted fluorescence **a** is observed, and the emitter is strongly polar [31].

Additional evidence, which can be considered a proof of the TICT state molecular and electronic structure, consists in following points: (i) radiative transition in emission is forbidden by a factor $10^{-3} - 10^{-2}$ [19] as expected for a zero orbital overlap of the mutually orthogonal D and A; (ii) transient absorption spectra (in the visible) of the polar excited state of DMABN [33] or of *p*- NMe_2 -benzaldehyde [34] match the absorption spectra of the respective radical anions, A^- (the absorption of the radical cation ($-\text{NMe}_2^+$) is outside of the studied spectral range).

Doubts and limitations

The TICT hypothesis seems to describe well the behaviour of simply substituted benzenes, pyrimidines (like those in Figs.1-4), and probably pyridines [36]. Doubts are arising when larger aromatic systems are involved. In the case of *p*-(9-anthryl)-*N,N*-dimethylaniline (ADMA), which in the excited state relaxes to a highly polar structure, apparently a

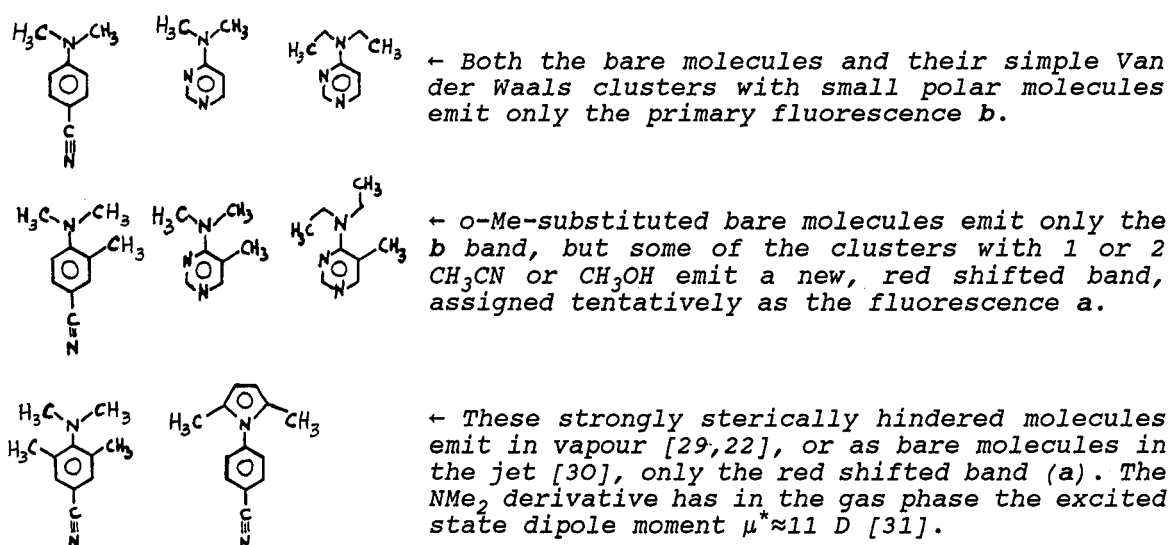


Fig.4. Results of study in supercooled jet [30]

TICT state [20], the transient absorption spectra of the singlet state are more complex than expected for a two-state system [37]. Recently Herbich and Kapturkiewicz, in their thorough study of a long series of ADMA, its derivatives, and other large aryl p-substituted N,N-dimethylanilines [38], found that both the allowed character of emission and the energetic considerations indicate the molecules relax to a state deviating from the 90° conformation. With increasing orbital overlap, the interactions with upper states may stabilize a partial CT state, both local and delocalized MO's contributing to the transition moment.

We find also deviations from a TICT behaviour in a series of acridines, substituted in position 10 by an alicyclic amino nitrogen, or by 4-N,N-dimethylaniline: their picosecond transient absorption spectra in polar solvents differ from both acridine radical anion and acridine excited singlet state [39].

Specially intriguing are the highly polar excited states of symmetric biaryls (nonpolar in their ground and primary excited states), the best known of which is 9,9'-bianthryl [40,41]. They were supposed to belong to the TICT states [9,22], but never it has been proved, e.g., by means of the model compounds. For 1,1'-bipyrene the excited state dipole moment appeared less than expected for a full ICT state [42].

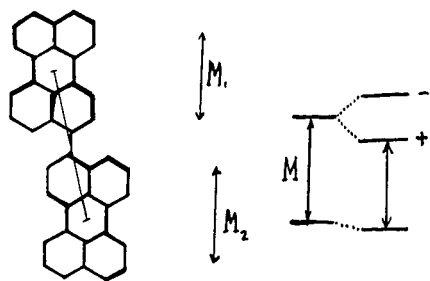


Fig.5. Biperylene excited state dipole moment is half as large as expected from the centre-to-centre distance [43].

The highest stabilisation energy of the TICT state was expected for 3,3'-biperylene [42]. Biperylene undergoes indeed in polar solvents a relaxation to the highly polar state, but its dipole moment is much less than that (≈ 41 D) which would correspond to a charge separation over a centre-to-centre distance in the large molecule [43] (Fig.5). The excitonic splitting is here large ($\sim M_1 M_2 / R^3$) and should be little dependent on the twist angle (M_1 and M_2 are large, parallel, shifted nearly along the vector M [44]). Most probably, the excitonic state allows a nonpolar component to the ICT state even at an orthogonal conformation.

FLUORESCENCE VS. POPULATION KINETICS

Most information on the very fast kinetics of the intramolecular ET and of the accompanying relaxation processes is known from the time-resolved rise and decay of the fluorescence signal, usually measured at a constant wavelength. Nonexponentialities are often reported, and the kinetics of the fluorescence **b** decay seem to differ from those of the rise of **a** [45].

In particular, for dimethylamino-indanone (upper right formula in Fig.2) in butyronitrile the rise of **a** is found to be markedly faster than the decay of the primary fluorescence **b**. We suspect that the fluorescence signal may not always be proportional to the real population of the emitting state. During the initial period of the reaction ($t < \tau_b$) the hypersurface minimum of the reaction product (Fig.6) is nearly empty. If (i) the fluorescence of the reaction product is forbidden (and such are

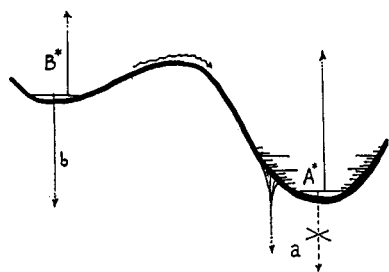
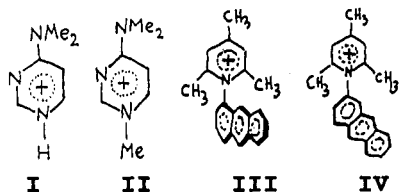


Fig.6. Scheme of a hot emission from the reaction path to the initially empty minimum A^* (from which the emission is forbidden). The reaction can be barrierless as well.

most often the TICT emissions [19]), (ii) the temporal resolution of the measurement is comparable to the average time of passage through the reaction path, (iii) the emission rate along the reaction coordinate is higher by orders of magnitude than in the final minimum - the observed signal may originate on the reaction path. This hot fluorescence signal will not be proportional to the population of the product state. The proportionality factor will be a function of time. One can test the real population kinetics by using parallelly an independent method; the picosecond time-resolved absorption spectra reveal in the case of dimethylamino-indanone the rise time of the population of A^* to be equal to that of the decay of B^* [46].

D-A⁺ MOLECULAR IONS



The remarkable feature of the D-A⁺ ions - whenever D and A⁺ can rotate, and the ET between them is energetically feasible - is their lack of fluorescence (e.g., I or II [32]) or, exceptionally only, very weak emission (as III and IV [47]). Radiationless deactivation is much faster than in analogous zwitterionic TICT states, formed

from the neutral molecules. As most deactivation paths of any ICT state are ET processes - the specificity seems to be searched in the kinetics of ET of the charge shift vs. charge recombination (e.g., [48]). The ICT states of D-A⁺ ions can deliver much evidence to the discussion on ET.

Acknowledgement

I express my thanks to the whole team of my past and present coworkers and coauthors for their friendly and stimulating cooperation. The work is done within the KBN grant 2-365-91-1.

REFERENCES

1. G.van der Zwan, J.T.Hynes, *J.Phys.Chem.* **89**, 4181 (1985).
2. A.Decléry, C.Rullière, *Chem.Phys.Lett.* **146**, 1 (1988).
3. Z.R.Grabowski, *Pure & Appl.Chem.* **64**, 1249 (1992).
4. A.Jabloński, *Acta Phys.Polon.* **6**, 350 (1937).
5. I.Rips, J.Klafter, J.Jortner, *J.Chem.Phys.* **89**, 4288 (1988).
6. J.Herbich, Z.R.Grabowski, J.Karpiuk, K.Yoshihara, N.Tamai, *J.Lumin.*, in press (1992).

7. W.M.Wiczak, T.Latowski, *Z.Naturf.* **41a**, 761 (1986); **42a**, 1290 (1987).
8. K.Rotkiewicz, K.H.Grellmann, Z.R.Grabowski, *Chem.Phys.Lett.* **19**, 315 (1973).
9. Z.R.Grabowski, K.Rotkiewicz, A.Siemiarczuk, D.J.Cowley, W.Baumann, *Nouv.J.Chim.* **3**, 443 (1979).
10. M.Polanyi, "Atomic Reactions"; Williams & Norgate; London (1932).
11. A.Weller, H.Staerk, R.Treichel, *Faraday Disc.Chem.Soc.* **78**, 271 (1984).
12. B.Wegewijs, R.M.Hermant, J.W.Verhoeven, A.G.M.Kunst, R.P.H. Rettschnick, *Chem.Phys.Lett.* **140**, 587 (1987).
13. B.Wegewijs, R.M.Hermant, J.W.Verhoeven, M.P.de Haas, J.M.Warman, *Chem.Phys.Lett.* **168**, 185 (1990).
14. H.Beens, A.Weller, in: "Organic Molecular Photophysics, J.W.Birks, ed.; Vol.II, p.321; J.Wiley & Sons, London (1975).
15. E.Lippert, W.Lüder, H.Boos, in: "Adv. in Molec.Spectroscopy", A. Mangini, ed.; p.443; Pergamon Press, Oxford (1962).
16. M.Kasha, *Faraday Soc.Disc.* **9**, 14 (1950).
17. E.C.Lim, *Excited States*, **3**, p.305; Academic Press, New York, 1977.
18. M.Van der Auweraer, *Academiae Analecta (Med.Konink.Acad.Weten., Lett.,Sch.Kunst.België) Kl.Wetensch.*, **48**,(6) 27 (1986).
19. M.Van der Auweraer, Z.R.Grabowski, W.Rettig, *J.Phys.Chem.* **95**, 2083 (1991).
20. A.Siemiarczuk, Z.R.Grabowski, A.Krówczyński, M.Asher, M. Ottolenghi, *Chem.Phys.Lett.* **51**, 315 (1977).
21. Z.R.Grabowski, K.Rotkiewicz, A.Siemiarczuk, *J.Lumin.* **18/19**, 420 (1979)
22. W.Rettig, *Angew.Chem.* **98**, 969 (1986).
23. P.Suppan, *J.Lumin.* **33**, 29 (1985).
24. Z.R.Grabowski, J.Dobkowski, *Pure & Appl.Chem.* **55**, 245 (1983).
25. V.Bonačić-Koutecký, J.Michl, *J.Am.Chem.Soc.* **107**, 1765 (1985).
26. Z.R.Grabowski, J.Dobkowski, W.Kühnle, *J.Molec.Struct.* **114**, 93 (1984)
27. J. Dobkowski, Z.R. Grabowski, *SPIE Proc.* **1683**, (1992), in press.
28. J.Herbich, F.Perez Salgado, R.P.H.Rettschnick, Z.R.Grabowski, H. Wójtowicz, *J.Phys.Chem.* **95**, 3491 (1990).
29. K.Rotkiewicz, W.Rubaszewska, *J.Lumin.* **27**, 221 (1982).
30. T.Kobayashi, M.Futakami, O.Kajimoto, *Chem.Phys.Lett.* **141**, 450 (1987)
31. H.Bischof, W.Baumann, N.Detzer, K.Rotkiewicz, *Chem.Phys.Lett.* **116**, 180 (1985).
32. J.Herbich, Z.R.Grabowski, H.Wójtowicz, K.Golankiewicz, *J.Phys.Chem.* **93**, 3439 (1989).
33. T. Okada, N. Mataga, W. Baumann, *J. Phys. Chem.* **91**, 760 (1987).
34. C.Rullière, Z.R.Grabowski, J.Dobkowski, *Chem.Phys.Lett.* **137**, 408 (1987).
35. Z.R.Grabowski, in: "Supramolecular Photochemistry", V.Balzani, ed.; p.319; Reidel, Dordrecht (1987).
36. J.Smagowicz, K.Berens, K.L.Wierzchowski, "Biological Molecules in Their Excited States", J.B.Birks,ed.; p.24; J.Wiley, New York (1976)
37. T.Okada, N.Mataga, W.Baumann, A.Siemiarczuk, *J.Phys.Chem.* **91**, 4490 (1987) .
38. J.Herbich, A.Kapturkiewicz, *Chem.Phys.* **158**,143 (1991); *ibid.* in press (1992).
39. J.Dobkowski, Z.R.Grabowski, J.Herbich, C.Rullière, to be published
40. F. Schneider, E.Lippert, *Ber.Bunsenges.Phys.Chem.* **72**, 1155 (1968); *ibid.* **74**, 624 (1970).
41. H.Beens, A.Weller, *Chem.Phys.Lett.* **3**, 666 (1969).
42. K.A.Zachariasse, private information (1976).
43. J.Dobkowski, W.Rettig, B.Paepflow, K.H.Koch, K.Müllen, R.Lapouyade, Z.R.Grabowski, submitted to *J.Am.Chem.Soc.*
44. Th.Förster, *Pure & Appl.Chem.* **4**, 121 (1962).
45. E.Lippert, W.Rettig, V.Bonačić-Koutecký, F.Heisel, J.A.Miehé, *Adv. Chem.Phys.* **68**,p.1; I.Prigogine, S.A.Rice,eds. Wiley, New York (1987)
46. J.Dobkowski, Z.R.Grabowski, C.Rullière, to be published.
47. V.A.Kharlamov, M.I.Knyazhansky, N.I.Makarova, V.A.Lokshin, *J.Photochem.Photobiol.* in press (1992).
48. T.Kakitani, N.Mataga, *J.Phys.Chem.* **90**, 993 (1986).