TWISTED INTRAMOLECULAR CHARGE TRANSFER (TICT) EXCITED STATES: ENERGY AND MOLECULAR STRUCTURE

Zbigniew R.Grabowski and Jacek Dobkowski

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

Abstract - Numerous compounds of donor (D) - acceptor (A)
type, in the excited singlet state undergo a relaxation to a
highly polar state, preferentially in fluid polar solvents.
Study of the rigid model molecules revealed the polar state
to correspond to the D and A moieties mutually twisted by
90°. To find another proof for the structure of the TICT
states, the energies of their emission were calculated for
18 molecules starting from the TICT model. The calculated
values are compared to the "polar" fluorescence maxima.
The correlation may serve as a structural proof for the TICT
states. The structural principle for these states seems to
involve a condition of minimum overlap between the D and A
orbitals involved in the electron transfer.

TICT STATES

Peculiar phenomenon of the dual fluorescence of p-cyanodimethylaniline 1
has been discovered two decades ago by Lippert and his students (1) . The
emission occurs from two different excited states, one of them being
strongly polar. Numerous attempts were published to explain the experimen-
tal results by a solvent-assisted inversion of states (Ref.1), by the
formation of excimers (Ref.2) or specific exciplexes with the polar solvent
molecules (Ref.3, 4) , by proton transfer (Ref.5) or by a high polarisabil-
ity of the excited state (Ref.6) . Another hypothesis tried to identify
the polar emitting state with the excited rotamer, its -N(CH$_3$)$_2$ group
being twisted by 90° with respect to the coplanarity with the aromatic ring
(Ref.7) . A full electron transfer had been assumed from the twisted amino
group to the aromatic moiety of the rotamer (Ref.8) . This model (Fig.1)
is gaining support specially by finding more and more D-A molecules
exhibiting similar behaviour (e.g., 2 - 18) . A convincing proof of the
structure of the polar emitting state is supplied by the fluorescence
spectra of model molecules with a structurally fixed flat or twisted
conformation, or sterically hindered to coplanarity, e.g. 19 (Ref.8, 9) ,
3 (Ref.9, 10) and 20 Ref.8, 11 as compared to 1, or 21 as compared to 8
(Ref.12) . Analogous comparisons, e.g. of 16, 22 and 23, indicated where
in the molecule does the internal rotation occur (Ref.13, 14) .

Fig.1 In the flexible D-A molecules a delocalisation of charge in
the coplanar conformation disappears in the conformation twisted by
90°. In the latter, the π electrons are localized either on D or on
A; the twisted ground state is often less polar than its planar
counterpart, while one of the lowest excited singlet states is
usually a zwitterionic state.

These highly polar emitting states have received a name of the twisted
intramolecular charge transfer (TICT) excited states (Ref.13, 15) . However
inadequate this name seems to be, we shall use it throughout this paper.
A survey of the earlier papers on the molecular and electronic structure,
dipole moments, spectroscopy, thermodynamics and kinetics of the TICT states
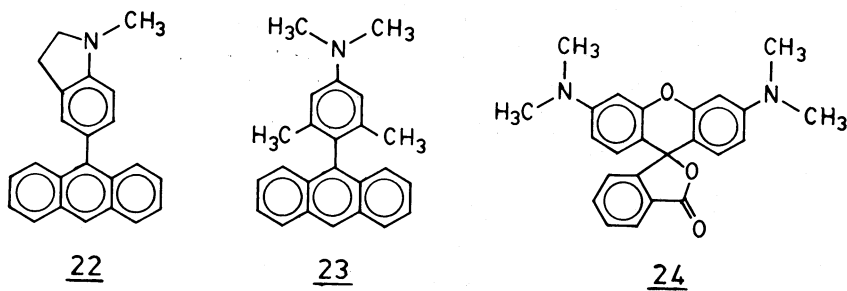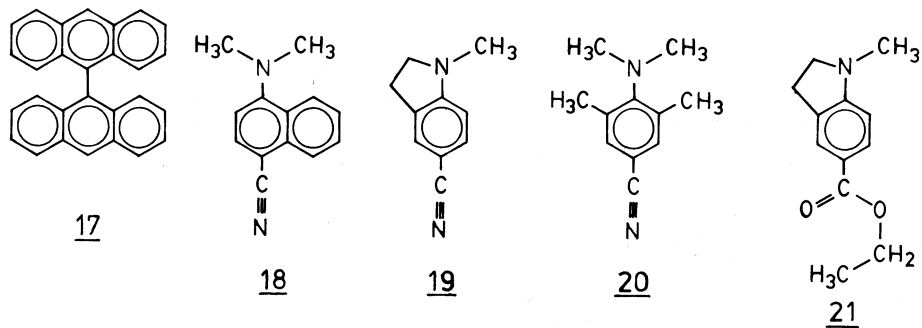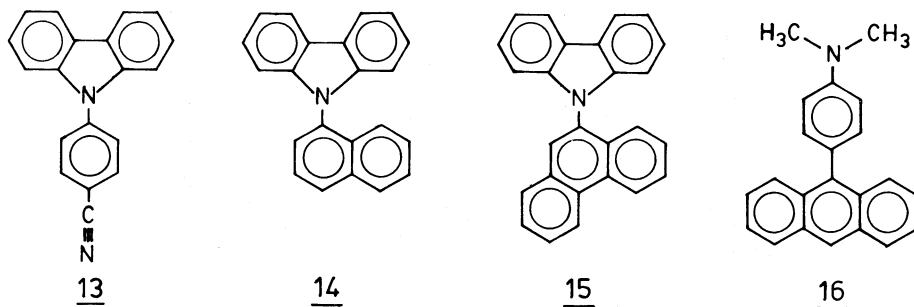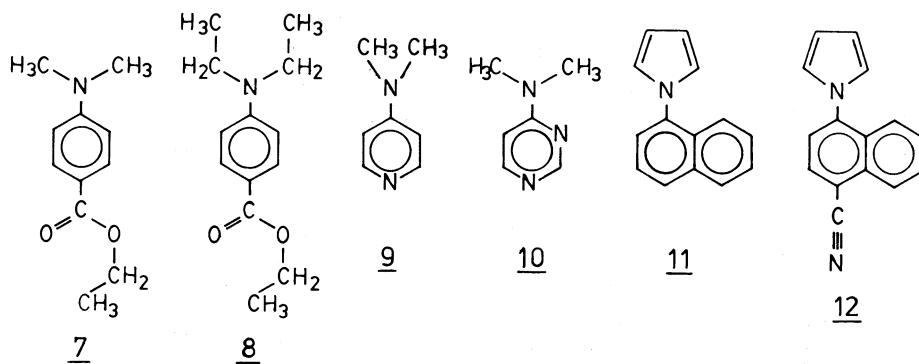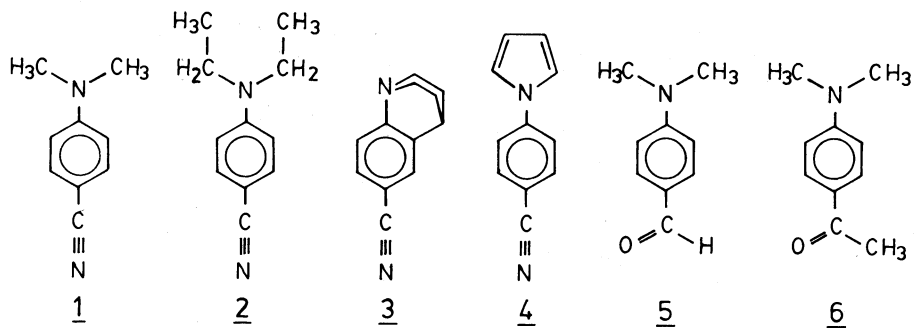
appeared in 1979 (Ref.9) . The evidence gained from the rapid development
of the kinetics of formation and decay of the TICT states (e.g. Ref.16-20)
or from the reactivity of the TICT states (Ref.21) will be left out of the
scope of this paper.

Since 1979 the TICT hypothesis has been put in doubt in several papers,
emphasizing either some specific interactions with the solvent (Ref.4) or
a high polarisability instead of a high permanent dipole moment (Ref.6,22).
Parallely, however, much of the experimental and theoretical evidence seems
to disperse these doubts. A TICT – type fluorescence is observed, e.g.
for 8 in inert hydrocarbon solvents (Ref.12) and for 20 even in the vapour
(Ref.11) . Several recent INDO or CNDO calculations (taking usually also
the solvation effects into account) supported the TICT state hypothesis in
the case of 1 (Ref.23,24) , 4 (Ref.25) , 5 (Ref.26) and 16 (Ref.14) .

The TICT states should be treated as intramolecular exciplexes with a
particular type of structure. Applicability of the corresponding energy
estimates may supply another proof for their supposed structures.

MODEL CALCULATIONS

To estimate the energy of a TICT state we treat it as a pair of radical
ions, $\overset{\bullet}{D}{}^{+}$ and $\overset{\bullet}{A}{}^{-}$, at a fixed distance (Fig.2) . We approximate the twisted
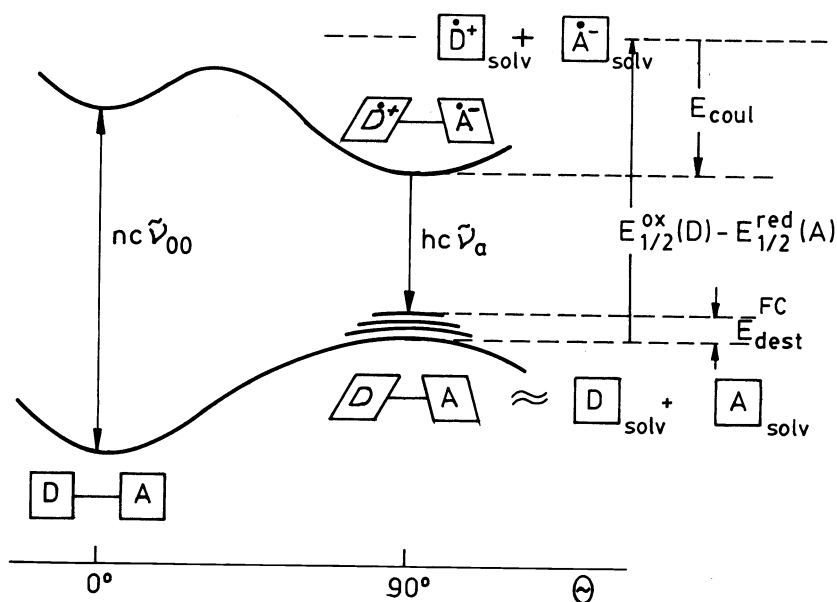

Fig.2 Scheme of the model calculation, for the originally flat
D–A molecules. In the case of those sterically hindered or with
fixed perpendicular structure (e.g. 3,16,17,20) the abscissae axis
has a modified meaning, while $hc\tilde{\nu}_{00}$ may mean a local excitation.

ground state D–A (the nonpolar alternative, Fig.1) by a sum of non intera-
cting solvated molecules D and A. Energy of the solvated radical ions,
$D^{+}_{solv} + A^{-}_{solv}$ is above that level by

$$E_{CT} = E^{ox}_{1/2}(D) - E^{red}_{1/2}(A) + T\Delta S_{o}. \tag{1}$$

The last term is expected to be roughly constant within the considered
series of compounds, temperature and solvent being kept constant. The
TICT state would lie lower, by a coulombic energy of bringing the opposite
charges to the fixed distance r (assuming the validity of the macroscopic
dielectric constant ε, and neglecting changes of solvation) :

$$E_{coul} = -e^2/r\varepsilon \tag{2}$$

The emission from this state (fluorescence band a) leads to the Franck-
-Condon (FC) state of the twisted ground state, i.e. to the nonpolar or

weakly polar state in the solvent environment oriented as around the
strongly polar TICT state. This FC state is more energetic than the
solvent-equilibrated ground state by the destabilisation energy (Ref.27) :

$$E_{dest} = (\vec{\mu}^{TICT} - \vec{\mu}^{G}_{FC})^2 \left[\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}\right]/a_o^3 \qquad (3)$$

Thus, the energy of the TICT fluorescence may be estimated as:

$$hc\tilde{\nu}_a = E_{CT} + E_{coul} - E_{dest}. \qquad (4)$$

The energetic condition for the TICT state formation will be:

$$hc\tilde{\nu}_{oo} > E_{CT} + E_{coul} + E_{barrier} \qquad (5)$$

where the last term denotes the height of the barrier to internal rotation
in the ground state.

CORRELATIONS

Treating the TICT state as a radical ion pair it was tempting to correlate
at first the observed fluorescence maxima with the difference of oxidation
and reduction potentials, $E^{ox}_{1/2}(D) - E^{red}_{1/2}(A)$, which proved so successful
in the study of intermolecular exciplexes (heteroexcimers) by Weller and
his students (28,29) . The values of the half-wave potentials are collec-
ted in Table 1. The correlation with emission energies in acetonitrile

TABLE 1.   Polarographic half-wave potentials of one electron oxida-
tion of the donors (D) and reduction of the acceptors (A) , in
acetonitrile solutions; Volts vs saturated calomel electrode.
Data from Ref.30 or 31.

Donor	$E^{ox}_{1/2}$ D	Acceptor	$-E^{red}_{1/2}$ A
N(CH$_3$)$_3$	1.05	benzonitrile	2.35
N(C$_2$H$_5$)$_3$	1.15	benzaldehyde	1.93
quinuclidine	0.97[a]	acetophenone	1.87
pyrrole	1.06	ethyl benzoate	2.32[b]
N-methyl--carbazole	1.1	pyridine	2.66
N,N-dimethyl--aniline	0.65	pyrimidine	2.34
		naphthalene	2.58
anthracene	1.14	1-cyano-naphthalene	2.00
[a]irreversible wave		phenanthrene	2.35
[b]in dimethylformamide		anthracene	2.00[b]

(r = 0.82) is unsatisfactory, substantially worse than those quoted
(Ref.28,29) , and with a low slope, 0.78. We tried therefore to apply the
eq.4. To obtain the data necessary for eqs. 2 and 3, we had to estimate
r, μ^{TICT}, μ^{G}_{FC}, and a$_o$ for the molecules 1 - 18. To establish the value of
r the centre of the positive charge is located at the nitrogen atom of D,
except 16 and 17, where it is placed in the centre of the donor ring. The
negative charge is located in the centre of the A ring (e.g. 10,11,16) ,
except those molecules where a farther shift of the charge is expected,
under the influence of a strong acceptor substituent in para position.
Thus, the centre of negative charge is centered close to the substituent,
at 3/4-th of the diameter of the A ring in all p-CN-derivatives and in
5 - 9. By definition μ^{TICT} = r·e. The dipole moment of the twisted ground
state, μ_{FC}, is the vector sum of the component moments for the mutually
twisted D and A (the values taken from the Ref.32) . For the -NR$_2$
groups zero is assumed unless there is a component from the lone pair on
the long molecular axis, as in 3. Every central C-N bond contributes by

0.5 D (Ref.32) . The Onsager cavity radius, a_o, is approximated by that of a sphere equal to molecular volume resulting from geometrical considerations, with intermolecular radii rounded up to 1.5 Å for H and to 2 Å for the C,N and O atoms (Ref.33) . The data are collected in Table 2, the correlation is shown in Fig.3.
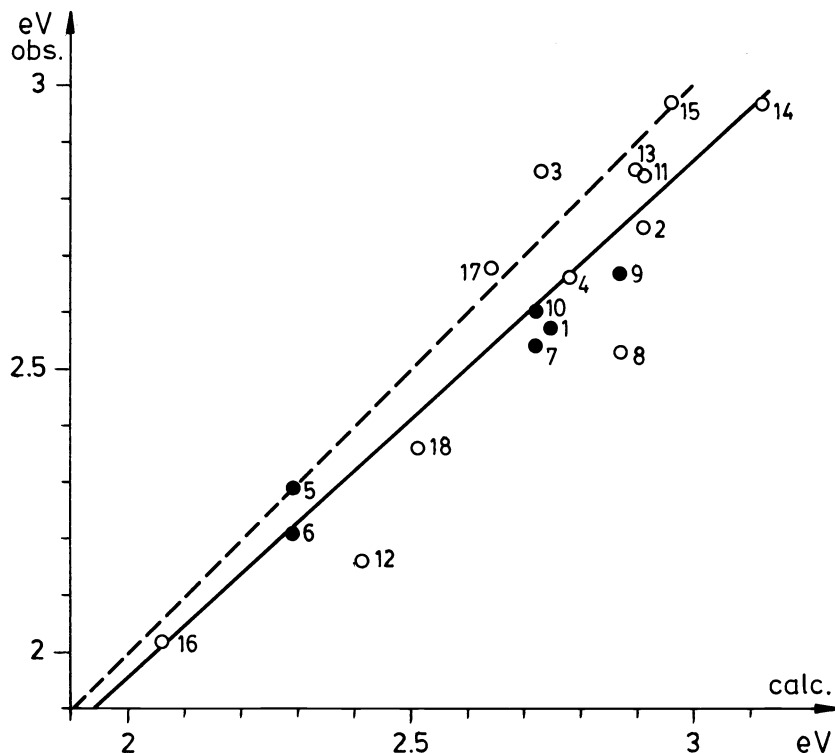

Fig.3 Energy of the a fluorescence maximum in acetonitrile, for the compounds 1 - 18, observed and calculated from the TICT model (Table 2) . Dashed line: equality of both values. Solid line: the best fit. Correlation coefficient r = 0.93. Solid points: molecules with identical donor group, $-N(CH_3)_2$. Correlation coefficient for these points: r'= 0.980.

The correlation according to eq.4 (Fig.3) has still a considerable spread of points. The regression line is:

$$hc\tilde{\nu}_{obs} = 0.145 + 0.91\ hc\tilde{\nu}_{calc}\ (\pm 0.1\ eV)\qquad\qquad (6)$$

Observed deviation from the unit slope may have no deep meaning. Limitation to the points with identical D improves the correlations much, both in Fig.3 and eq.(4). Taking into account the experimental errors and the roughness of approximations done, we consider the correlation to be another proof of the adequacy of the TICT model.

MINIMUM OVERLAP RULE ?

The number of compounds behaving similarly to those described above is quite large. The compounds 1 - 18 have been chosen because of availability of the necessary data, and they are a representative sample. There are, however, other molecules, nonpolar or weakly polar in the ground state, which emit from a state characterized by a full intramolecular charge transfer, and which have no possibility to internally rotate.

One of these rigid structures is represented by 3, composed of the mutually perpendicular D and A moieties. Something similar is found in the case of

TABLE 2. Model parameters and the calculated and observed energies of the fluorescence $\underline{a}$ transition $(hc\tilde{\nu}_a)$ for the molecules $\underline{1}$ - $\underline{18}$ in CH_3CN solutions

no	μ^{TICT} (D)	μ^G_{FC} (D)	a_o^3 (Å³)	$-E_{coul}$ (eV)	E_{dest} (eV)	$hc\tilde{\nu}_a$ calc. (eV)	$hc\tilde{\nu}_a$ obs. (eV)	Ref.
1	17.3[a]	3.5[b]	67	0.11	0.54	2.75	2.57	1
2	17.3	3.5	76	"	0.48	2.91	2.75[c]	35
3	17.3[d]	3.2	78	"	"	2.73	2.85	10
4	17.3	1.8	68	"	0.52	2.78	2.66	36
5	17.3[e]	2.5	72	"	0.58	2.29	2.29	37
6	17.3	"	80	"	0.52	2.29	2.29	38
7	"	1.4	89	"	0.58	2.72	2.54[f]	16
8	"	"	98	"	0.49	2.87	2.53	12
9	"	1.7	64	"	0.73	2.87	2.67	39
10	13.9	2.2	"	0.13	0.54	2.72	2.60	40
11	"	-2.2	81	0.11	0.61	2.91	2.84	25
12	17.3	1.8[g]	85	"	0.54	2.41	2.26	"
13	"	1.9[h]	103	"	0.44	2.90	2.85	42
14	13.9	-2.6[h]	117	0.13	"	3.11	2.97	"
15	"	"[h]	139	"	0.37	2.95	2.97	"
16	20.6[j]	1.6	136	0.09	0.50	2.06	2.07	14
17	"	0	194	"	0.41	2.64	2.68	43
18	17.3	3.5[g]	84	0.11	0.43	2.51	2.36[i]	44

(a) to be compared to calculated (INDO) values: 16.4 D (Ref.23) , 14 D (Ref.24) or to experimental 16.2 D (Ref.9) and a series of alternatives: 20, 16.7, 5.8 or 8.1 D (Ref.6) .   (b) calculated values: 3.5 D (CNDO, Ref.34) , 4.5 D (INDO, Ref.24) ; experimental 0.7 D (Ref.9,6) .   (c) in n-BuCl.   (d) exp. 13 ÷ 15 D (Ref.10) . (e) calc. 15.2 D (INDO, Ref.26) .   (f) in EtOH.   (g) assuming μ(1-CN-Naphthalene) = μ(Benzonitrile) .   (h) μ(Carbazole) = = -2.1 D (Ref.41) .   (i) in n-BuCN.   (j) calc. 20.3 D (INDO, Ref.14) ; exp. 18 D (Ref.45) , 15.2 D (Ref.9) and 17.9 D for $\underline{22}$, 19.3 D for $\underline{23}$ (Ref.9; compare, however, Ref.22) .

the spirofuran derivative, rhodamine B lactone $\underline{24}$. Its dipole moment increases with excitation to the fluorescent state by 25 D (Ref.46) which may reflect a large distance of the electron transfer. We can predict a similar behaviour in numerous other spirocompounds.

9,9'-Bianthryl $\underline{17}$ represents symmetrical systems, in which D=A. $\underline{17}$ undergoes a polar solvent induced intramolecular electron transfer (Ref.43,47) . The compound is in its ground state in a twisted by 90° conformation. A similar behaviour of 1,1'-bipyrenyl has been observed (Ref.48) . Remarkably, Mataga et al (49) observed an analogous solvent-induced electron transfer in [2.2] (1,3) pyrenophane $\underline{25}$ where the two identical π-electronic systems are not perpendicular; they are parallel but shifted away.

An intermediate case is represented by the compound $\underline{26}$, in which the anthracene and anthrone moieties are nearly perpendicular, and a CT fluorescence is emitted in polar solvents (Ref.50) . Another intermediate case may be expected in the symmetrical flexible 1,2-di (9-anthryl) ethane where a formation of a CT intermediate is inferred from the fluorescence behaviour (Ref.51) .
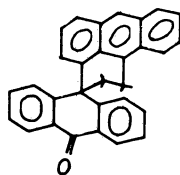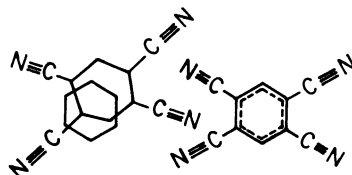
$\underline{25}$ $\underline{26}$ $\underline{27}$ $\underline{28}$

Theory for the solvent-induced polarisation in symmetrical molecules, involving an interplay of excimer and CT structures, is founded by Beens and Weller (52) .

We find now a **remarkable structural requirement**, common for all TICT and analogous intramolecular CT states mentioned above. It is a m i n i m u m o v e r l a p between the donor and acceptor molecular orbitals involved in the electron transfer (Ref.9) . This empirical rule contrasts to the generally accepted maximum overlap rules derived by Mulliken (53) for weakly polar ground state CT complexes. Present rule awaits still its theoretical justification.

There are two important points to be discussed in the context of the empirical minimum overlap rule noted for the TICT states.

(i) Bonačić-Koutecký et al.   (54) developped the theory of a s u d d e n p o l a r i s a t i o n on twisting various unsaturated systems around their originally double bond. Closely around 90° twist the biradical structure is replaced by a zwitterionic structure. In spite of all existing differences in the MO description of the sudden polarisation and of the TICT state formation (Ref.55) , both have in common striking similarities in the observables and in the underlying physics (Ref.56) .

(ii) The TICT excited states, as well as the polar excited states of the type of 24 or 26, are examples of intramolecular exciplexes with certain structural restrictions preventing them to acquire, e.g., a sandwich structure. The observed structural principles should be, however, particular cases of the rules governing the structure of exciplexes. The well known benzene – TCNB complex, having the structure 27 in the ground state, relaxes in the excited state to the apparently maximum overlap structure, 28. Nagakura (57) noted that for this high symmetry structure the overlap integral between the electron donating and accepting orbitals is zero. How far this may be a hint for other exciplexes with a practically full intramolecular CT ? The theory comprising the TICT states and the symmetrical biaryl-type molecules as particular cases of exciplexes is needed.

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