Concerning medium polarity effects on the photophysics and photochemistry of TICT-forming dyes

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Abstract

Mechanism and dynamics of the excited state relaxation in compounds able to form TICT states were investigated from a theoretical point of view with special reference to the dielectric solvent effects. The study included 4-dimethylamino-4'-cyanostilbene (DCS) and Michler's Hydrol Blue (MHB), which are thought to involve emitting and non-emitting TICT states, respectively. It was found that in DCS the formation of TICT states, by twisting either the dimethylamino or the dimethylanilino groups, may in principle be induced by the solvent polarity but requires extreme conditions. In MHB, both calculations and new fluorescence quantum-yield measurements in a variety of solvents indicated that the TICT-state formation is essentially controlled by the solvent viscosity.

1. INTRODUCTION

According to the model first introduced by Grabowski et al. [1], a "Twisted Intramolecular Charge Transfer" (TICT) compound is usually schematized as a coplanar bichromophoric system composed of one electron-donor (D) and one electron-acceptor (A) moieties connected by an essentially single bond. Photoexcitation of such a system creates a "locally excited" (LE) partial CT state which relaxes, at a rate depending on the polarity and viscosity of the solvent, into a perpendicular arrangement of the two moieties characterized by full CT. During the last decade TICT-forming compounds have attracted great interest [2] as suitable molecular models in connection with light-induced charge separation processes occurring in both technologically and biologically important systems. Let us recall molecular electronic devices [3] on the one hand and the visual process or photosynthesis [2] on the other.

Light-induced formation of TICT states can manifest itself by two seemingly opposite behaviours. One is the appearance of an anomalous dual fluorescence in polar solvents. Dimethylaminobenzonitrile (DMABN) provides the most classic example of fluorescent TICT state [1] (Fig.1). In this case the involvement of the orthogonally twisted conformation was supported by the absence of the longer-wavelength emission, attributed to TICT, in synthesized model compounds where the dimethylamino group was rigidly held in the planar position [4,5].

By replacing the dimethylamino group with a p-dimethylaminostyryl group, DMABN changes into 4-dimethylamino-4'-cyanostilbene (DCS) which can be considered as a prototype of the donor-acceptor stilbene derivatives (Fig.2).

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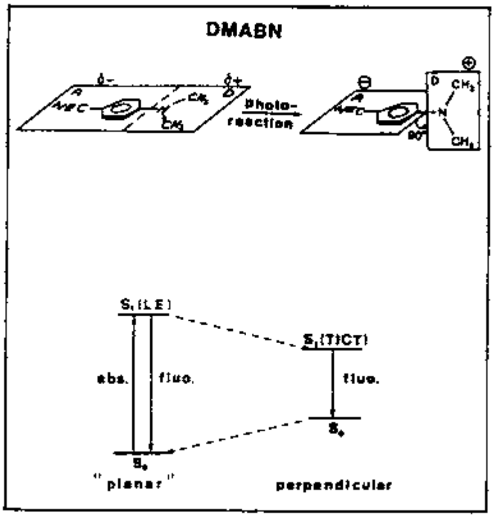


Figure 1. Model of the excited-state relaxation of DMABN involving a full - CT fluorescent state with orthogonal arrangement of the donor [$N(CH_3)_2$] and acceptor [C_6H_4CN] goups [1].

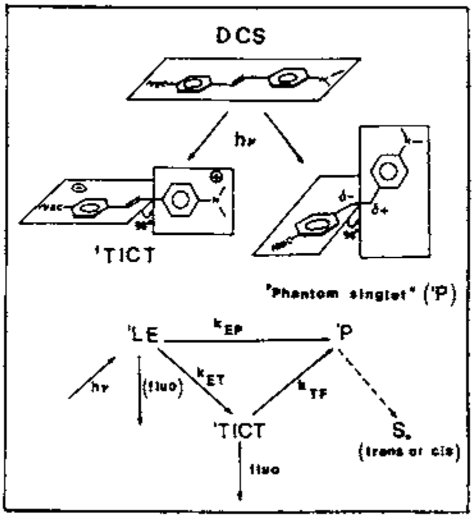


Figure 2. Molecular model and kinetic scheme [6] of the excited-state relaxation of DCS involving competing formation of the double-bond twisted (^{1}P) and a single-bond twisted (^{1}TICT) states.

In these compounds the relaxation of the LE state may occur by twisting about one of the single bonds, leading to formation of a TICT state, or by twisting about the double bond towards the stilbene-type "phantom singlet" state. In contrast with stilbene, these dyes possess a strong fluorescence whose properties (unusually large Stokes shift and strong red-shift with increase in the solvent polarity) are consistent with a TICT nature of the emitting state [6]. Moreover, in contrast again with the normal stilbene derivatives, their photoisomerization efficiency decreases when the polarity of the solvent increases. Rettig and Majenz [6] interpreted this anomalous polarity behaviour in terms of competition between the "phantom singlet" and TICT formation processes. According to these authors, in polar solvents the TICT state can be sufficiently stabilized so as to act as a photochemical trap reducing the photoisomerization yield and enhancing the fluorescence emission.

The formation of a TICT-like state has also been invoked to account for the fast nonradiative decay of certain dyes in fluid solutions. Contrary to what happens in the cases mentioned before, this type of TICT state is nonemissive and is thought to act as an efficient intramolecular fluorescence quencher. As relevant examples of systems able to form short-lived nonluminescent TICT states, we may recall the diphenylmethane (DPM) and triphenylmethane (TPM) dyes, such as Crystal Violet (CV) [7] (Fig.3).

Two main observations must be made in this case:

- Firstly, these systems are cations and the twisted excited state is characterized by full localization of the positive charge on the donor part, instead of a real charge separation.

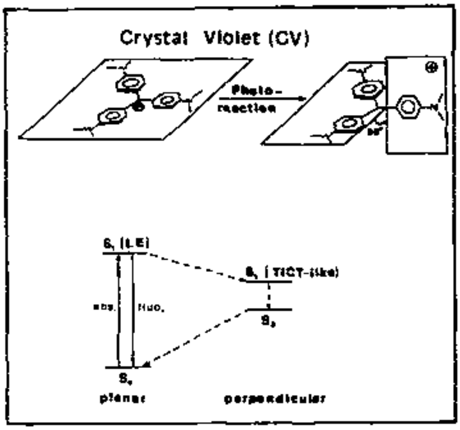


Figure 3. Model of the excited - state relaxation of Crystal Violet [7] involving a low-lying non-fluorescent TICT-like state.

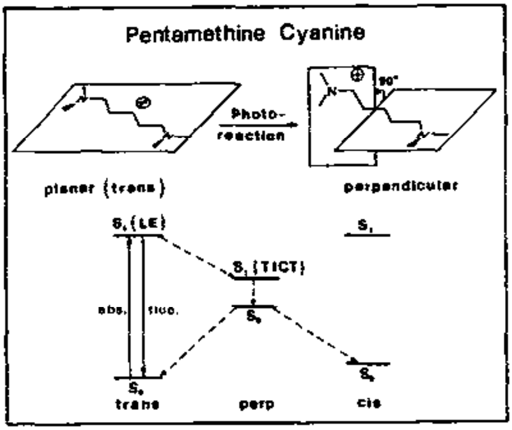


Figure 4. Model of the excited-state relaxation of a polimethine cyanine [9] involving *trans* → *cis* isomerization via a low-lying TICT-like state.

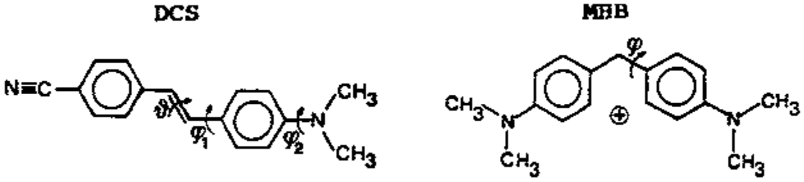
- Secondly, the perpendicular geometry is attained not by twisting of a dimethylamino group but by twisting of a dimethylanilino group as a whole, as shown by the strong fluorescence of ring-bridged model compounds as well as by the dependence of the deactivation rate on the size of the rotor [7].

Recent quantum chemical calculations on Michler's Hydrol Blue (MHB) (a typical DPM dye) [8] have clearly confirmed that such a TICT state can really be formed following $S_0 \rightarrow S_1$ excitation. Moreover, similar theoretical calculations had previously shown [9] that the same type of TICT state is involved in the nonradiative excited-state decay of cationic open-chain cyanine dyes (Fig.4). Of course in this case internal quenching of the fluorescence results not only in ground state recovery, as in TPM and DPM dyes, but also in the formation of a *cis* isomer. In other words, this is an example of TICT state acting as a photoreaction intermediate.

In the present paper we report a new theoretical study on DCS and MHB, taken as examples of compounds thought to be able to form luminescent and nonluminescent TICT states, respectively. Calculations were devised for the dual purpose of locating the TICT states and establishing to what extent electrostatic solute-solvent interactions may favour the TICT-state formation with respect to the other deactivation processes of the LE state. On this basis we will attempt to draw some conclusions about the validity of the proposed mechanisms (Fig.s 2,3). For MHB we report new fluorescence quantum-yield measurements in solvents of very different dielectric constants and viscosities, which will be shown to fit the theoretical predictions very well.

2. CALCULATION PROCEDURE

The overall objective of the theoretical study was approached in two steps. The first was the calculation of the potential energy curves for the twisting motions of the isolated molecule in the ground and lowest excited states (Scheme 1).



Scheme 1

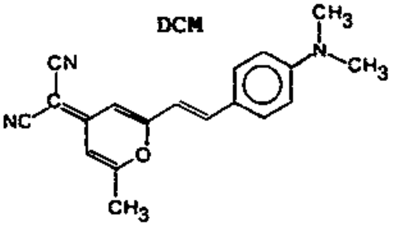
MO SCF calculations were carried out by the CS INDO method [10] which has proved to be suitable for studying electronic spectra and conformational rearrangements of conjugated non-rigid molecules [8,9,11].

The electron correlation effects were introduced by a second order perturbative CI technique [12] starting from multiconfigurational wavefunctions obtained in turn by variational treatment of a proper zeroth-order subspace. In the case of DCS the zeroth-order space included all the monoexcitations from the 9 highest occupied (HO) to the 7 lowest virtual (LV) molecular orbitals (MOs), and all the doubly excited configurations involving the three HO and the three LV MOs. This choice was prescribed by the need to start from a correct zeroth-order description of both the single- and double-bond twisting in the parent compound (unsubstituted stilbene). The various internal rotations were performed according to a rigid rotor model starting from standard geometries of the planar forms, with the only exception of the ethylenic bridge for which we adopted a relaxed structure (r_{c-c}=1.43 and $r_{c=c}$=1.38 Å) especially suitable for the state S_1. For MHB we did not perform new calculations, but we simply used the results of a recently published CS INDO CI study [8] in order to evaluate the solvent-induced changes (see ref. [8] for all details).

In the second step, the solvation energies were evaluated state by state according to the virtual charge (or solvaton) model first proposed by Klopman [13] and subsequently improved by Heidrich et al. [14]. In practice we adopted a slightly modified version of Heidrich's formula:

$$E_{sol} = -0.5\,(1 - D^{-1})\,[\,\Sigma_A Q_A^2/R^{eff} + \sum_{A\neq B}\Sigma\, Q_A Q_B/(r_{AB} + R^{eff})\,] \qquad (1)$$

where D is the static dielectric constant of the solvent, R^{eff} is an average effective atomic radius, r_{ab} is the distance between the centres of the atoms A and B, and Q_A (Q_B) is the net charge on the atom A (B) derived by the zeroth-order CI treatment of the isolated molecule. The energy of the solvated molecule was taken as equal to its energy in the gas phase (D=1) plus the solvation energy E_{sol}. Very recently, Marguet et al. [15,16] applied this model to the DCM styrene dye (Scheme 2), and showed that, when dealing with large molecules, it works better than the "macroscopic" models, derived from the reaction field of Onsager [17], which are based on the global dipole moment of the solute.



Scheme 2

3. FLUORESCENCE QUANTUM YIELD MEASUREMENTS

This investigation was limited to MHB where the fluorescence quantum yield may be assumed to be roughly complementary to the quantum yield of the LE → TICT process, in the absence of additional efficient channels for the nonradiative deactivation of the LE state (see Fig. 3).

MHB in CH_2Cl_2 was employed as the reference system. Its fluorescence yield has been amended from $2.5x10^{-4}$ [8] to $3.0x10^{-4}$ as a consequence of the recent correction of the quantum yield of Cresyl Violet [18], that was used as the reference system in our previous determination. Measurements were carried out on a JY3CS Jobin Yvon spectrofluorimeter at 21-22° C. Chlorobenzene (RPE Carlo Erba, passed through an activated alumina-silica gel column) was the least polar solvent in which MHB dissolved sufficiently. The other solvents - dichloromethane (Merck, UVASOL), methanol (Merck, p.a.) and glycerol (RPE, Carlo Erba) - were used without further purification. All of them showed no significant emission in the adopted experimental conditions. The viscosities of the water-glycerol mixtures were measured at 20° C with a capillary viscometer, pure glycerol being taken as the reference system (1490 cP) [19]. The viscosities of pure solvents, as well as their dielectric constants and refractive indexes (which entered into the calculations of the fluorescence quantum yields), were taken from ref. [20]. As for the water-glycerol mixtures, their refractive indexes were evaluated from the pure component ones using the Lorentz-Lorenz expression and their dielectric constants were interpolated from the data of ref. [21].

4. RESULTS AND DISCUSSION

4.1. Trans-4-dimethylamino-4'-cyanostilbene (DCS)

The DCS study presented here parallels a recently reported theoretical study on a DCS analogue, the DCM dye [15,16] (Scheme 2). We recall that in ref.s [15,16] the theoretical approach, combining the CS INDO MR (multireference) CI calculation of the intramolecular potential energy curves with the use of eq. (1) for the dielectric solvent effects, was first successfully tested on DMABN where the direct relationship between the solvent dependent fluorescence behaviour and the formation of a TICT state has been most firmly established. Briefly, it was found that the S_1 state of the fully twisted conformation (Fig. 1), which correlates with the S_2 (^1L_a - type) state of the planar form, has very strong CT character and in highly polar solvents (e.g. in CH_3CN, D=37.5) its energy becomes markedly lower than that of the LE state. With $R^{eff} = 4$ a.u. in eq. (1), the theoretical description conformed very well to the model proposed by Grabowski et al. [1] (Fig.1). On the other hand, in DCM, where the main excited-state deactivation channel is the trans → cis isomerization, the calculation results did not provide conclusive evidence for the formation of an emitting TICT state. In fact, the TICT state was found to be the second singlet-excited state of the single-bond twisted DCM in the gas phase. High polar solvents caused inversion of the S_1 and S_2 states but the TICT state remained above the LE state, unless $R^{eff} < 4$ a.u. was used. However, the S_1-S_2 inversion resulted in an increase of the barrier impeding relaxation of the LE state towards the photochemical funnel (^1P), thus suggesting that formation of the TICT state, if possible, may result in a reduction of the *trans* → *cis* photoisomerization yield as experimentally observed [22]. Finally, only the twisting of the dimethylamino group was found to result in the formation of a strongly CT state.

With the extension of the theoretical treatment to DCS we attempted to establish to what extent the photophysical properties of DCM are similar to those of more common donor-acceptor stilbene derivatives.

First we analysed the twisting of the double bond ($\vartheta = 0°$ to $90°$) by keeping both the dimethylamino and the dimethylanilino groups, assumed as the possible donors, in their coplanar conformation ($\varphi_1 = \varphi_2 = 0°$) (Fig.5).

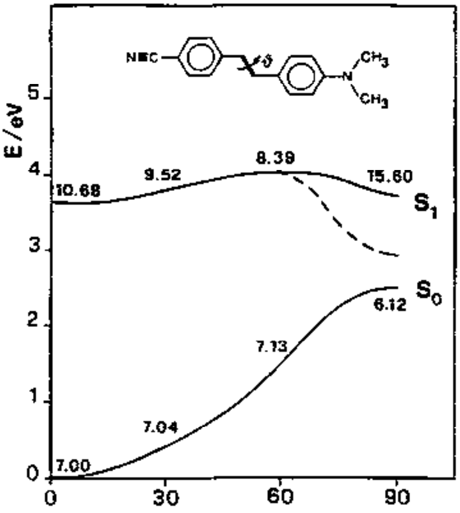


Figure 5. Potential energy curves describing the 0° to 90° double - bond twisting in the S_0 and S_1 states of DCS in the gas phase (D=1) (—) and in a polar solvent (D=40) (----). Numbers on the potential curves indicate the dipole moment values in debyes.

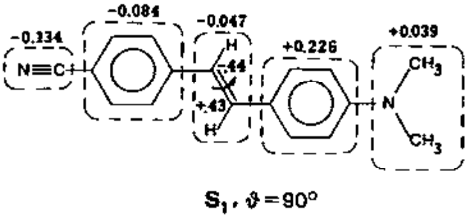


Figure 6. Global net charges on the different molecular subunits and zwitterionic character of the double-bond twisted S_1 state of DCS .

The potential energy curves obtained for the gas-phase molecule (full lines) approximately reflect the theoretical model generally accepted for the double-bond twisting of stilbene and its derivatives. However, unlike stilbene [23] and DCM [15,16] the perpendicular configuration does not correspond to the absolute minimum of the S_1 potential curve. The analysis of the net charges on the different molecular subunits showed that the state S_1, in spite of the rather high dipole moment (Fig. 5), does not present any appreciable CT character either in the planar or in the perpendicular geometry (Fig. 6). On the other hand, the twisted excited state has zwitterionic character as evidenced by the large polarization of the central double bond (Fig.6), so it is identifiable as the stilbene-like "phantom singlet"*. In view of the dipole moment increase around the perpendicular geometry, polar solvents should be expected to cause an appreciable relative stabilization of the "phantom singlet" state. In fact, Fig. 5 shows that the solvation effect manifests itself as a marked

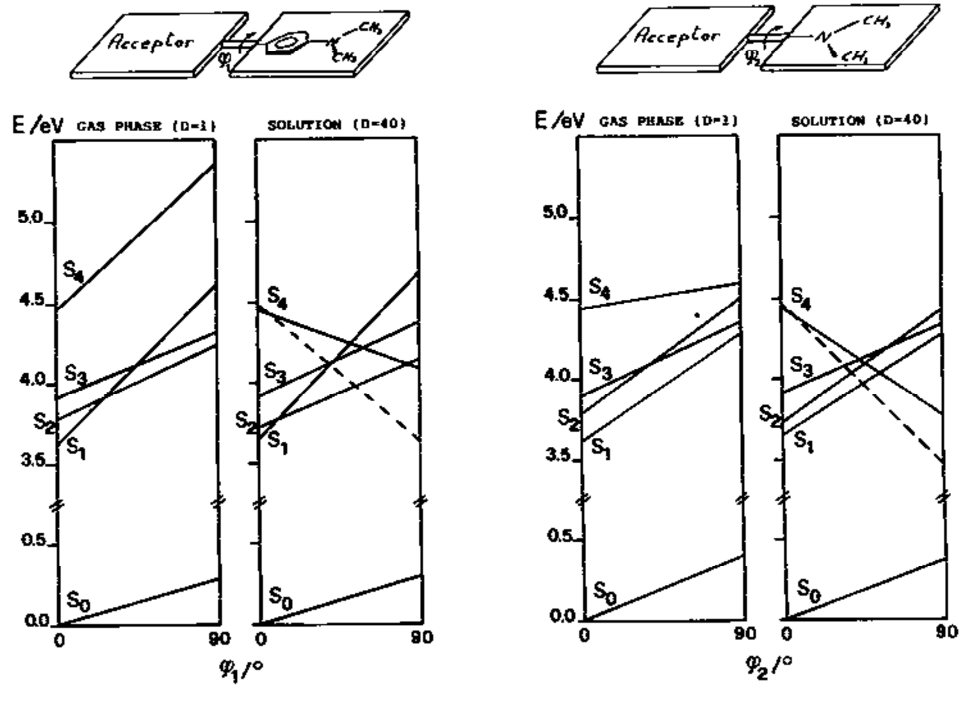


Figure 7. Effect of the solvent polarity on the energy correlation diagrams for the lowest-lying singlet states of DCS in the planar and 90° twisted conformations of the dimethylanilino (φ_1=90°) and dimethylamino (φ_2=90°) groups. Dotted lines show the effect of using R^{eff} = 3 a.u. instead of 4 a.u. in eq. (1).

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* We note that this description is very similar to that obtained in ref [15] for double-bond twisted DCM, while it is in contrast with recent CNDO/S CI calculations on DCS [24] and DCM [25], according to which the 90° twisted conformation should be characterized by weakly polar S_1 and strongly polar S_0 states.

lowering of the S_1 potential energy (dotted line) around the perpendicular configuration (ϑ=90°) which becomes the absolute minimum of the S_1 surface. From Fig. 5 it is evident that solvation does not affect the barrier impeding double-bond twisting, so the anomalous decrease of the photoisomerization efficiency in high polar solvents can only be due to the opening of a second relaxation channel competing with isomerization.

In order to check whether TICT formation may be such a channel, we analysed the changes in energy (Fig.7) and charge distribution (Tables 1 and 2) of some lowest singlet states on passing from the coplanar to the orthogonal arrangement of each donor group. The main observation is that twisting of the

Table 1.
Charge distributions and dipole moments of the ground state and the lowest excited singlet states of planar DCS.

	$\theta=\varphi_1=\varphi_2=0°$				
	S_0	S_1	S_2	S_3	S_4
$N(CH_3)_2$	-.028	+.054	+.088	-.006	+.154
Benzene ring	+.092	+.128	-.120	+.111	+.037
Double bond	-.050	-.043	+.017	+.098	-.141
Benzene ring	+.085	-.033	+.113	-.150	+.049
CN	-.099	-.106	-.097	-.053	-.100
μ (debye)	7.00	10.68	6.21	9.53	12.13

Table 2.
Charge distributions and dipole moments of the ground state and four lowest singlet-excited states of DCS with twisted dimethylanilino (φ_1=90°) or dimethylamino (φ_2=90°) groups.

	$\varphi_1=90°$					$\varphi_2=90°$				
	S_0	S_1	S_2	S_3	S_4	S_0	S_1	S_2	S_3	S_4
$N(CH_3)_2$	-.040	-.013	+.150	-.042	+.125	-.100	-.094	-.084	-.098	**+.741**
Benzene ring	+.076	+.061	-.146	+.084	**+.804**	+.148	+.201	+.044	+.180	**-.545**
Double bond	-.026	+.065	-.002	+.088	**-.596**	-.045	-.009	+.021	+.085	-.093
Benzene ring	+.088	-.026	+.096	-.089	-.209	+.093	-.006	+.115	-.120	+.020
CN	-.098	-.086	-.098	-.041	-.123	-.097	-.093	-.095	-.047	-.123
μ (debye)	6.27	7.56	7.99	6.87	**25.98**	5.58	7.32	3.94	7.50	**21.04**

donor groups induces substantial changes in the charge distribution of the excited states. This is especially true for the fourth excited state which, in the fully twisted geometry, attains an unusually high dipole moment related to a very large internal charge transfer. So in both cases the TICT state is identifiable as the fourth single-bond twisted excited state. When the molecule is dissolved in a medium of high polarity the TICT states become the lowest excited states, thus complying with the primary condition for a TICT emission. The larger solvent effect occurs for the dimethylanilino-twisted CT state (φ_1=90°), but the lower lying TICT state is that formed by twisting of the dimethylamino group (φ_2=90°). However, both TICT states remain above the LE state when E_{sol} is calculated by the usual parametrization (R^{eff} = 4 a.u.) and may be forced to become lower than the LE state only by reducing the value of R^{eff} (see dotted lines in Fig. 7). These results do not authorize us to say that in polar solvents the LE state can really decay to a TICT emitting state.

The theoretical description provided by Fig. 7 for DCS is similar to that obtained in ref.s [15,16] for DCM with two minor differences: 1) the state S_4 of DCS behaves like the state S_2 of DCM , this being traceable to their composition (in both cases [HOMO-1, LUMO] and [HOMO^2, LUMO^2] are the predominant configurations), and 2) unlike DCM, in DCS internal twisting of both the dimethylamino and dimethylanilino groups leads to formation of highly polar TICT states.

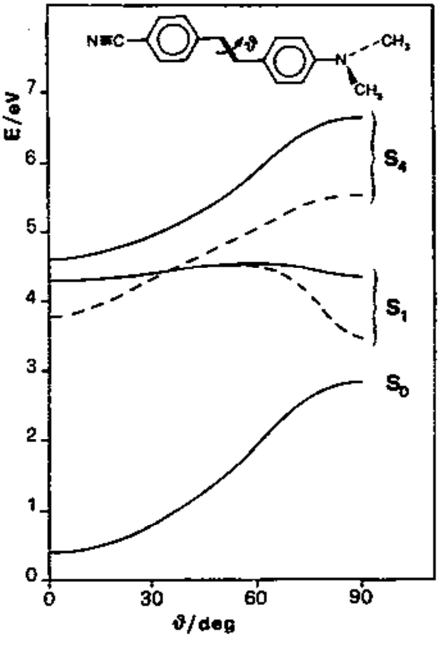

Figure 8. Potential energy curves describing the double-bond twisting of DCS in the S_0 and S_1 states for the perpendicular conformation of the $N(CH_3)_2$ group: (——) in the gas phase (D=1) (from ref. 8); (-----) in a polar solvent (D=40).

In order to learn more about the interrelation between the decay processes via ^{1}TICT and ^{1}P states (Fig.2), we re-calculated the potential energy curves for the twisting about the double bond by keeping the donor group in its fully orthogonal arrangement. The dimethylamino group, giving rise to the TICT state of lower energy (Fig.7), was taken as the electron donor in this test calculation (Fig.8). As is evident, the potential energy diagram of Fig. 8 is almost superimposable on that of Fig.5, obtained with the coplanar arrangement of the donor group, as far as the S_0 and S_1 potential curves are concerned. In particular, the solvent polarity effect is represented by a deepending of the photochemical funnel (^{1}P) potential well. On the other hand, in this case the potential energy curve of the state S_4 (the TICT state) undergoes a marked solvent-induced lowering, related to the above discussed state inversion (Fig.7), which results in the creation of a substantial barrier hindering $^1LE \rightarrow ^1P$ isomerization. In summary, Fig. 8 indicates that, in the case where the TICT state is formed by effect of the solvent polarity, relaxation via the photochemical funnel becomes unfavoured. This result matches that obtained in ref.s [15,16] for DCM , and gives some support to the hypothesis that TICT formation and *trans* →*cis* isomerization are competing channels in the excited-state deactivation of donor-acceptor-type stilbene derivatives in highly polar solvents [6,24].

4.2. Michler's Hydrol Blue (MHB)

An extensive discussion on this diphenylmethane dye has already been reported in ref. [8]. Here, we simply recall that in contrast with the parent base (Ph-CH_2-Ph), which prefers non-planar helical-type conformations in fluid solutions [26], MHB is essentially planar with a π-electron conjugation extended over the whole molecule in keeping with the notion of dye. Thus, MHB may be thought to consist of nonamethine-cyanine subchromophores as shown in Fig. 9. This interpretation is supported by several considerations of

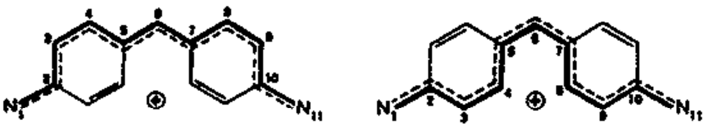

Figure 9. Modelling of π electronic structure of MHB in terms of two nonamethine cyanine subchromophores.

both the experimental and theoretical type. As an example, MHB and the assumed parent cyanine, bisdimethylaminononamethine cyanine (BMNC), have very similar visible-absorption bands ("colour" bands) (MHB: λ_{max}=607.5 nm, log ε=5.17 in 98% CH_3COOH [27]; BMNC: λ_{max}=625 nm, log ε=5.47, in CH_2Cl_2 [28]). Moreover, all the π and π* MOs of MHB, apart from two orbital pairs localized on the hexatomic rings (named vinyl-type orbitals by Platt), can easily be shown to correspond one-to-one to the π MOs of BMNC. The similarity is particularly close for the HOMO (essentially non-bonding) and LUMO orbitals involved in the excitation responsible for the "colour" band: a

90° twisting about one of the central bonds leads to formation of two decoupled π fragments with seven and eight atoms. In this conformation, where HOMO and LUMO become localized on the "odd" and "even" fragments, respectively, (Fig. 10a), the HOMO-LUMO transition gives rise to a TICT-like excited state characterized by localization of the positive charge on the "odd" fragment. As is already known [9], exactly the same occurs in the parent cyanine (Fig. 10b).

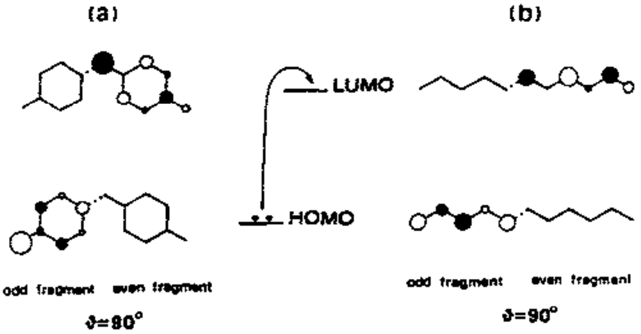

Figure 10. Localization of the frontier π MOs in the perpendicular conformation of MHB (a) and the parent nonamethine cyanine (b) and CT nature of the HOMO-LUMO excitation.

Going on with this analogy, the ground and excited state potential curves for the twisting of MHB about one of its central bonds are expected to be like the ones describing the *trans* →*cis* isomerization of a simple cyanine [9]. In particular, the TICT-like excited state should correspond to a distinct minimum on the S_1 surface, also existing in the isolated molecule, easily reachable from the locally excited state by overcoming of a small barrier. In fact, the results of our recent CS INDO CI study [8] of the MHB internal rotation conform well to the cyanine model (Fig. 11, full lines), even if the excited state minimum appears to be rather flatter. The CT nature of the intramolecularly twisted excited state is emphasized by Fig. 12 showing the global net charges of the donor- and acceptor-acting groups along with the most significant net atomic charges. It is evident that the positive charge is localized on the "odd" (donor-acting) fragment in the excited state and on the "even" (acceptor-acting) fragment in the ground state. Dielectric solvent effects are expected to come into play around the perpendicular form, due to the charge-localization phenomenon, whereas they should only poorly affect the potential energy curves near the planar conformation. This is what has really been found at the theoretical level when introducing the solvation effects (Fig. 11). It must be pointed out, in particular, that the solvent causes a marked energy stabilization of the state S_1 in the TICT region while the conversion from the planar to the perpendicular form appears to be an essentially barrierless process in all cases. To be more precise, the small barrier found for the gas phase molecule seems to disappear when the solvent polarity becomes higher and higher. Anyway, some 50% of the limit solvent effect is already operative in solvents of low dielectric constant.

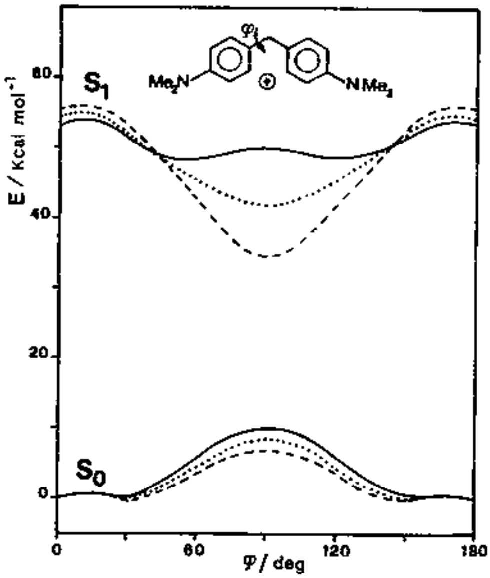

Figure 11. Twisting potential energy curves for the S_0 and S_1 states of MHB in the gas phase (D=1) (——), in a not very polar solvent (D=2) (····) and in a highly polar solvent (D=40) (----).

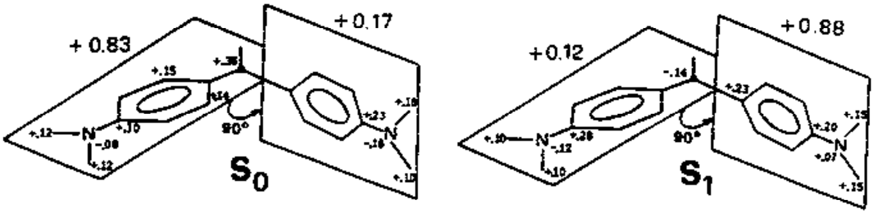

Figure 12. Charge distributions in the S_0 and S_1 states of twisted (φ=90°) MHB.

In conclusion, contrary to the case of luminescent TICT states, like that occurring in DMABN, the intramolecular quenching via non-luminescent TICT states should be little dependent on the solvent polarity. On the other hand, the process involves internal rotation of a rather bulky group, so its rate should be strongly controlled by the solvent viscosity. That this prediction is right, is clearly demonstrated by the fluorescence quantum yields of MHB^+,Cl^- measured in three solvents of very different polarities, but similar and low viscosities and in a series of glycerol-water mixtures of very different viscosities (Table 3). As is evident, in fluid solutions the fluorescence quantum yield is very low and undergoes just a small reduction when the dielectric constant of the solvent increases from 5.6 to about 33. On the other hand, the quantum yield increases rapidly as the solvent viscosity increases and in pure glycerol it is about two orders of magnitude higher than that observed with the methanol solution.

Table 3.
Solvent polarity and viscosity dependence of the fluorescence quantum yield of MHB^+,Cl^- measured at 21 °C.

Solvent	ε	η(cP)	$10^4 \cdot \Phi_{FM}$
Chlorobenzene	5.62	0.80	4.7
Dichloromethane	8.93	0.45	3.0
Methanol	32.7	0.60	2.0
Glycerol:H_2O ^{a}			
60:40	59.4	13	8.2
70:30	55	26	12.3
80:20	50	63	18.9
90:10	46	249	37.6
95:5	43.6	551	73.4
Glycerol (100:0)	42.5	1490	115.5

^{a} Nominal v/v ratios

5. CONCLUDING REMARKS

Although the TICT-state model first proposed by Grabowski et al. [1] has subsequently been tested and generalized by accurate calculations on simple model systems [29], explicit calculations on dyes of practical interest have hitherto been very scanty. Thus, considering the growing importance of TICT compounds for investigating photoinduced intramolecular charge separation, we have attempted to provide a comprehensive quantum chemical description of the excited-state relaxation for a donor-acceptor stilbene dye (DCS) and a diphenylmethane dye (MHB), which are thought to involve a luminescent and a nonluminescent TICT state, respectively.

The present investigation, following a previous study of DCM [15,16], was based on CS INDO CI calculations of the ground and excited state potential curves and charge distributions of the isolated molecule and on the use of a simple virtual-charge model for the evaluation of the solvation energy. Generally speaking, the calculation recipe proved to be a suitable tool for dealing with the photophysics of complex dye systems in solution. As regards the specific dyes considered here, the main conclusions are as follows:

1) In DCS the TICT state, obtained by twisting either the dimethylamino or the dimethylanilino groups, is just the fourth singlet-excited state in the gas phase (D=1). In a highly polar solvent (D=40) such states become the lowest

excited states of the twisted conformation, but their formation remains unfavoured for energy reasons, unless more drastic solute-solvent interactions are postulated. Interestingly, the formation of the TICT state, should it be possible, results in a reduction of the *trans* → *cis* isomerization rate in keeping with the observed effect of the solvent polarity.

2) For MHB the calculation results indicate that the TICT state, corresponding to the lowest, essentially HOMO-LUMO, singlet-excited state of the perpendicular conformation, can be efficiently formed also in solvents of very low polarity. So the MHB photophysics is expected to be influenced by the solvent viscosity, because of the drag forces opposing the internal twisting of the dimethylanilino group, much more than by the medium polarity. The validity of this prediction was confirmed by new measurements of the fluorescence quantum yield in solvents of expressly chosen polarity and viscosity characteristics.

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REFERENCES

1 Z.R. Grabowski, K. Rotkiewicz, A. Siemiarczuk, D.J. Cowley and W. Bauman, Nouv. J. Chim. 3 (1979) 443.
2 W. Rettig, Angew. Chemie 98 (1986) 969; Angew. Chem. Internat. Ed. Engl. 25 (1986) 971.
3 W. Rettig, Appl. Phys. B 45 (1988) 145.
4 G. Wermuth and W. Rettig, J. Phys. Chem. 88 (1984) 2729.
5 W. Rettig and R. Gleiter, J. Phys. Chem. 89 (1985) 4676.
6 W. Rettig and W. Majenz, Chem. Phys. Letters 154 (1989) 335.
7 M. Vogel and W. Rettig, Ber. Bunsenges. Phys. Chem. 89 (1985) 962.
8 I. Baraldi, A. Carnevali, F. Momicchioli and G. Ponterini, Chem. Phys. 160 (1992) 85.
9 F. Momicchioli, I. Baraldi and G. Berthier, Chem. Phys. 123 (1988) 103.
10 F. Momicchioli, I. Baraldi and M.C. Bruni, Chem. Phys. 82 (1983) 229.
11 I. Baraldi, G. Ponterini and F. Momicchioli, J. Chem. Soc. Faraday II 83 (1987) 2139; G. Bartocci, F. Masetti, U. Mazzucato, A. Spalletti, I. Baraldi and F. Momicchioli, J. Phys. Chem. 91 (1987) 4733; F.Momicchioli, I. Baraldi and E. Fisher, J. Photochem. Photobiol. A48 (1989) 95; F. Momicchioli, I. Baraldi, G. Ponterini and G. Berthier, Spectrochim. Acta 46A (1990) 775.
12 B. Huron, J.P. Malrieu and P. Rancurel, J. Chem. Phys. 58 (1973) 5745.
13 G. Klopman, Chem. Phys. Letters 1 (1967) 200.

14 D. Heidrich, U. Goering, W. Forster and C. Weiss, Tetrahedron 35 (1979) 651.

15 S. Marguet, J.C. Mialocq, P. Millié, G. Berthier and F. Momicchioli, Chem. Phys. 160 (1992) 265.

16 S. Marguet, D. Sc. Thesis, University of Paris Sud, n. 1936, 23 January 1992 (CEA, CE Saclay).

17 A.T. Amos and B.L. Burrows, Advan. Quantum Chem. 7 (1973) 289.

18 S.J. Isak and E.M. Eyring, J. Phys. Chem. 96 (1992) 1738.

19 Handbook of Chemistry and Physics, R.C. Weast, Ed., CRC Press, Cleveland, 1975.

20 S.L. Murov, Handbook of Photochemistry, M. Dekker, New York, 1973.

21 G. Åkerloef, J. Am. Chem. Soc. 54 (1932) 4128.

22 M. Meyer, J.C. Mialocq and M. Rougee, Chem. Phys. Letters 150 (1988) 484; M. Meyer, J.C. Mialocq and B. Perly, J. Phys. Chem. 94 (1990) 98.

23 G. Orlandi and W. Siebrand, Chem. Phys. Letters 80 (1975) 352; G. Orlandi, P. Palmieri and G. Poggi, J. Am. Chem. Soc. 101 (1979) 3492.

24 W. Rettig, W. Majenz, R. Lapouyade and G. Haucke, J. Photochem. Photobiol. A62 (1992) 415.

25 W. Rettig, private communication.

26 I. Baraldi, E. Gallinella and F. Momicchioli, J. Chim. Phys. 83 (1986) 653.

27 C. Aaron and C.C. Barker, J. Chem. Soc. (1963) 2655.

28 J. Fabian and H. Hartmann, Light Absorption of Organic Colorants, ch. 12, Springer, Berlin, 1980.

29 E. Lippert, W. Rettig, V. Bonačić-Koutecký, F. Heisel and J.A. Miehé, Advan. Chem. Phys. 68 (1987) 1.