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Comment on “Pseudo-Jahn–Teller and TICT-models: a photophysical comparison of *meta*- and *para*-DMABN derivatives” [Chem. Phys. Lett. 305 (1999) 8]  
The PICT model for dual fluorescence of aminobenzonitriles

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**Abstract**

Due to the larger admixture of charge transfer (CT) in the intramolecular charge transfer (ICT) state than in the locally excited (LE) state of dual fluorescent molecules such as 4-(dimethylamino)benzonitrile, the radiative rate constant  $k_f(\text{ICT})$  is smaller than  $k_f(\text{LE})$ , irrespective of the ICT molecular structure. The validity of the TICT or PICT model can therefore not be tested with these data. The absence of dual fluorescence for 4-(methylamino)benzonitrile, 3-(dimethylamino)benzonitrile and two dicyano-*N,N*-dimethylanilines, which cannot be explained by the TICT hypothesis, is caused by their large energy gap  $\Delta E(S_1, S_2)$ , which prevents the ICT state from becoming lower in energy than LE. © 2000 Elsevier Science B.V. All rights reserved.

**1. Introduction**

In a recent Letter, Rettig et al. [1] reported spectral and photophysical properties of a series of *meta*- and *para*-substituted aniline derivatives. These data were presented in an attempt to differentiate between their twisted intramolecular charge transfer (TICT) model [2,3] and two other models for the dual fluorescence observed with 4-(dimethylamino)benzonitrile (DMABN) and related molecules [4–9]. In particular, the radiative rate constants  $k_f(\text{LE})$  and

$k_f(\text{ICT})$  of the locally excited (LE) and the intramolecular charge transfer (ICT) state of aminobenzonitriles and esters of aminobenzoic acid were discussed on the basis of the  ${}^1L_b/{}^1L_a$  concept, without considering the contribution from charge transfer (CT) states. In addition, the reasons for the absence of dual fluorescence in the case of the *meta*-substituted anilines such as 3-(dimethylamino)benzonitrile (*m*-DMABN) were treated. As our model for the ICT reaction of DMABN [5–9] is in our view misinterpreted in Ref. [1], this comment serves the purpose of presenting a discussion of the significance of  $k_f(\text{LE})$  and  $k_f(\text{ICT})$  in connection with the structure of the ICT state of the aminobenzonitriles. Also, the predictive capabilities of the TICT and

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PICT models with respect to the occurrence or nonoccurrence of dual fluorescence will be examined. For clarification, first an outline of the essential aspects of the TICT, RICT and PICT models and also of the  ${}^1L_b/{}^1L_a$  nomenclature will be given.

## 2. Discussion

### 2.1. TICT, RICT and PICT. Statements on the structure of the ICT state

The dual fluorescence of DMABN, observed in solvents more polar than alkanes [3,10,11], consists of emissions from an aniline-like initially excited LE state and from an ICT state, for which LE is the precursor [11,12]. The TICT model in its essence makes a statement on the structure of the equilibrated ICT state, assuming that in this state the dimethylamino group of DMABN is twisted into a plane perpendicular to that of the benzonitrile moiety. The RICT [4] and the PICT [6–9] models likewise define the molecular structure of the ICT state. In these acronyms, R and P stand for ‘rehybridised’ and ‘planar’, referring to a bent and hence rehybridised cyano group and to an essentially planar molecule, similar to a quinoidal resonance structure [7,10,13], respectively. Arguments pro [4,14] and contra [15–17] the RICT model, as well as experiments on which the PICT model is based [6–9], can be found in the literature. As Rettig et al. concentrate their model comparison on TICT and PICT [1], only these models will be further discussed here.

In the PICT model, independent of the structure of the ICT state, a small energy gap  $\Delta E(S_1, S_2)$  between the two lowest excited singlet states is considered to be an important requirement for the occurrence of dual fluorescence [5–9]. In this connection, the terms vibronic coupling and pseudo-Jahn–Teller coupling have been used [5,6]. For a discussion focused on the structure of the ICT state, TICT should be confronted with the structural aspects of PICT and not in the first place with an approach such as vibronic coupling (Section 2.3), which primarily addresses the dynamics of the LE  $\rightarrow$  ICT reaction, which is not an integral part of the TICT hypothesis.

### 2.2. The ${}^1L_b/{}^1L_a$ concept

The nomenclature  ${}^1L_b$ ,  ${}^1B_b$  and  ${}^1L_a$  has been introduced for unsubstituted alternant aromatic hydrocarbons such as benzene and naphthalene [18]. For these molecules, the ‘forbidden’  ${}^1L_b$  state is the lowest singlet state  $S_1$ , whereas the more ‘allowed’  ${}^1L_a$  state is  $S_2$  [19]. The  ${}^1L_b$  concept is based on the symmetrical arrangement of the occupied and unoccupied molecular orbitals. When the symmetry is destroyed by substitution, such as in toluene or methylnaphthalenes, this concept is no longer strictly valid and  ${}^1L_b$  is mixed with  ${}^1L_a$  for  $S_1$  and vice versa for  $S_2$ . Apart from this  ${}^1L_b/{}^1L_a$  mixing, the presence of the electron donor (D) and acceptor (A) substituents in the case of DMABN leads to the appearance of substantial CT character [20,21], especially in the  ${}^1L_a$  state.

### 2.3. Short- and long-axis polarisation. Vibronic coupling

The  $S_1$  state of DMABN still retains some aspects of the  ${}^1L_b$  state of benzene, because of its polarisation along the short molecular axis, perpendicular to the direction of the D/A-substituents [13]. We therefore use the notation  $S_1({}^1L_b)$  [11], notwithstanding its considerable dipole moment (9–10 D [22]). In the  $S_2$  state, in contrast,  ${}^1L_a$  is strongly mixed with CT, both being long-axis polarised. The polarisation spectra of DMABN [13] reveal that the red edge of the absorption spectrum ( $S_1$ ) is polarised in the short axis of the molecule ( ${}^1L_b$ ), whereas the main absorption band ( $S_2$ ) is long-axis polarised ( ${}^1L_a$ , CT). A similar mixed polarisation is observed for the LE fluorescence in ethanol at 77 K [13]. A short-axis polarisation is detected at the blue edge of the spectrum, while the main LE fluorescence band is polarised in the direction of the long axis. This non-uniform polarisation of the LE emission does not indicate that there are two fluorescence bands, but shows that vibronic coupling between  $S_1({}^1L_b)$  and  $S_2({}^1L_a, CT)$  is an important phenomenon in this molecule [23]. Note that the observation that the absorption and LE fluorescence bands of DMABN are both long-axis polarised at their maxima does not by itself constitute a reason to conclude that the

Lippert model (level inversion of  $S_1(^1L_b)$  and  $S_2(^1L_a, CT)$ ) is incorrect, a conclusion that led to the introduction of the TICT model [24], as the short-wavelength edge of the LE fluorescence band is in fact short-axis polarised.

#### 2.4. Radiative rate constants $k_f(LE)$ and $k'_f(ICT)$

In Ref. [1], the values for  $k'_f(ICT)$  of DMABN and the corresponding ester derivative in acetonitrile are compared with  $k_f(LE)$  data of a series of anilines not showing dual fluorescence. As discussed in the previous section, the LE and ICT states and hence their radiative rate constants  $k_f(LE)$  and  $k'_f(ICT)$  are determined by different admixtures of the  $^1L_b$ ,  $^1L_a$  and CT zero-order states. Pure CT states, such as present in intermolecular exciplexes  $^1(A^-D^+)$ , have small  $k'_f$  values (of the order of  $10^7 \text{ s}^{-1}$ ), mainly due to the large difference in CT character of the exciplex as compared with its Franck–Condon (FC) ground state (AD) [25–27]. As the dipole moment (17 D) and therefore the CT character of the ICT state of DMABN and other dual fluorescent D/A-benzenes is considerably larger than that of LE (9–10 D) and the ground state (6.6 D) [22,28], it is not surprising that also for DMABN  $k'_f(ICT)$  is smaller than  $k_f(LE)$ , with values of  $1.9 \times 10^7$  and  $5.7 \times 10^7 \text{ s}^{-1}$  in toluene at 25°C, respectively [9].

#### 2.5. PJT model

It follows from the previous sections that the model termed PJT in Ref. [1] does not represent our view on the photophysics of DMABN. The PJT scheme discussed there is not applicable to a D/A-substituted benzene such as DMABN, for which CT interactions play an important role. In fact, it only holds for molecules with weakly perturbing substituents, such as alkyl-substituted aromatic hydrocarbons, with singlet excited states without an appreciable CT character. Such states are not stabilised in polar solvents, unlike what is the case for the  $S_1$  and  $S_2$  states of DMABN [5,10,13]. This means that a conclusion on the applicability of either the TICT or the PICT model cannot be derived from a comparison of  $k_f(LE)$  and  $k'_f(ICT)$ , as the difference between these radiative rate constants reflects that the ICT state has a more pronounced CT character and

hence a larger dipole moment than the LE state, an experimentally well-established fact on which no difference of opinion exists [22,28].

#### 2.6. PICT model

In our PICT model, different from PJT, the  $S_2(^1L_a, CT)$  state has a substantially larger dipole moment than  $S_1(^1L_b)$  [5,6], which preferentially decreases its energy relative to that of  $S_1(^1L_b)$  upon increasing the solvent polarity, see Figs. 1 and 1, b. When the energy gap  $\Delta E(S_1, S_2)$  is sufficiently small [6,7], a dynamic state reversal can occur after excitation, leading to an emitting ICT state alongside LE, and dual fluorescence appears (Fig. 1b). During the reaction from LE to ICT, changes in the molecular structure take place, involving the configuration of the amino nitrogen as well as the bond lengths in the molecule [5–9], which changes will contribute to the magnitude of the ICT reaction barrier  $E_a$  and the destabilisation energy  $\delta E_{FC}$  of the FC ground state reached after the ICT fluorescence (Fig. 1b). When the ICT state is considered to be correlated with  $S_2(^1L_a, CT)$ , on the basis of the similarity of their polarisation directions, the energy difference  $\Delta E(S_1, S_2)$  will determine whether the condition  $E(CT) < E(S_1)$  can be fulfilled or not, see Fig. 1.

#### 2.7. Predictions from the TICT model. $E(CT)$

The assumption of the TICT model that in the ICT state of DMABN the dimethylamino group is located in a plane perpendicular to that of the benzonitrile moiety does by itself not offer the possibility to predict whether for a particular molecule dual fluorescence will occur or not. When, however, the electronic decoupling of the amino and benzonitrile moieties of DMABN, as required by the TICT model, would in fact take place in the ICT state, then it would be possible to calculate its energy  $E(CT)$  from the redox potentials  $E(D/D^+)$  and  $E(A^-/A)$  of these D and A moieties and the Coulomb energy  $C(A^-D^+)$ , see Eq. (1) [6,7,9,29]. The ICT state is thereby considered to be similar to a weakly coupled intermolecular exciplex  $^1(A^-D^+)$ , a logical consequence of the TICT model and its principle of minimum overlap [2,3]. A calculation of  $E(CT)$  could then serve to test whether the energy of the

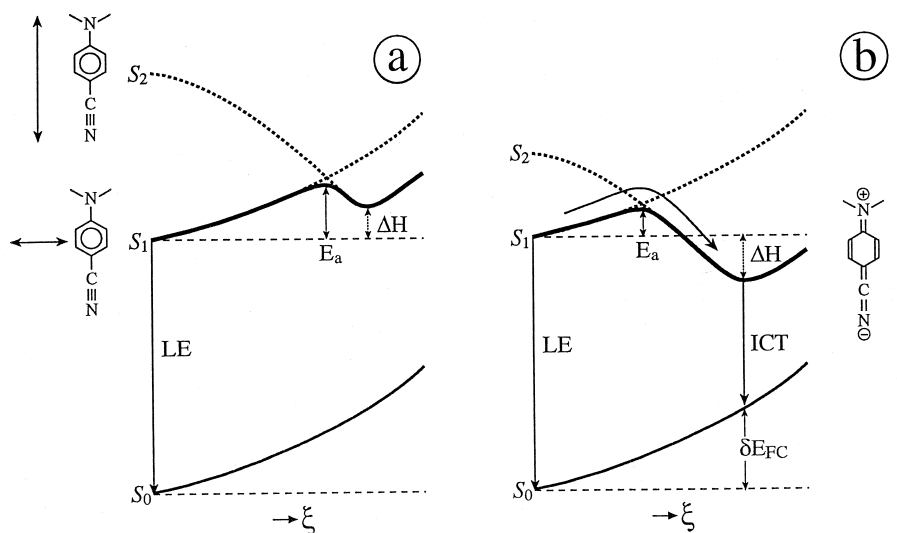


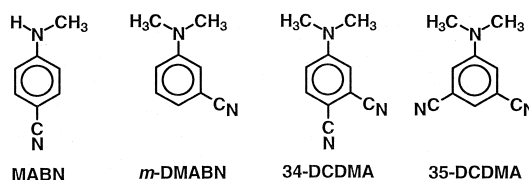
Fig. 1. Representation of the planar intramolecular charge transfer (PICT) model, for two energy gaps  $\Delta E(S_1, S_2)$ , depicting the ICT reaction of a potentially dual fluorescent molecule such as 4-(dimethylamino)benzonitrile (DMABN). The reaction coordinate  $\xi$  involves changes in the configuration of the amino group (towards planarity) and in the bond lengths. Dual fluorescence occurs when  $\Delta E(S_1, S_2)$  is sufficiently small to allow the energy of the ICT state to become lower than that of  $S_1$  (b). The directions of the transition dipole moments of the  $S_1$ ,  $S_2$  and ICT states have been drawn next to the molecules. The strongly polar character of the ICT state is represented by a quinoidal resonance structure.  $\Delta H$  is the enthalpy difference between the LE and ICT states. In (b),  $E_a$  is the activation energy for the ICT reaction depicted by a curved arrow and  $\delta E_{FC}$  is the energy difference between  $S_0$  and the Franck–Condon ground state reached by ICT emission.

ICT state is lower than that of LE, an essential requirement for the occurrence of an ICT reaction. The applicability of Eq. (1) for dual fluorescent systems such as DMABN has been employed as a diagnostic tool for the verification of the TICT hypothesis [29].

$$E(\text{ICT}) = E(\text{D}/\text{D}^+) - E(\text{A}^-/\text{A}) + C(\text{A}^-\text{D}^+). \quad (1)$$

It has been shown for a series of 4-(dialkylamino)benzonitriles, however, that the linear relation (slope unity) between  $E(\text{ICT})$  and the difference  $E(\text{D}/\text{D}^+) - E(\text{A}^-/\text{A})$  as required by Eq. (1) does not hold [9]. From the slope between 0.1 and 0.3 thereby obtained, it was concluded that the amino and benzonitrile groups are strongly coupled in the ICT state of DMABN, in accordance with the PICT model, but in clear conflict with the TICT hypothesis.

## 2.8. No dual fluorescence with MABN, *m*-DMABN, 34-DCDMA and 35-DCDMA



With 4-(methylamino)benzonitrile (MABN), dual fluorescence is not observed, even not in polar solvents such as acetonitrile [5–9]. This cannot easily be understood within the context of the TICT model (Eq. (1)), as the increase in oxidation potential  $E(\text{D}/\text{D}^+)$  of  $\sim 0.3$  V brought about by the exchange from the dimethylamino (DMABN) to the methylamino group (MABN) would be more than

overcompensated by the substantial lowering of  $E(\text{ICT})$  by  $\sim 0.8$  eV, due to the ICT dipole moment of 17 D [22], when going from an alkane solvent to acetonitrile [6,11]. In addition, the difference of around 0.1 eV between the energies  $E(S_1)$  of MABN and DMABN [5,9] would lead to a further increase of  $-\Delta G$  for the LE  $\rightarrow$  CT reaction by this amount.

For *m*-DMABN as compared with DMABN, again from the point of view of the TICT model (Eq. (1)), two factors should lead to a decrease of  $-\Delta G$  for the ICT reaction. First, as correctly pointed out in Ref. [1], the energy of the LE state of *m*-DMABN in acetonitrile is  $\sim 0.5$  eV lower than that of DMABN in this solvent. Taking into account the stabilisation of 0.8 eV for the ICT state in acetonitrile relative to *n*-hexane discussed above, the remaining  $-\Delta G$  of  $\sim 0.3$  eV would still be sufficient to allow an ICT reaction to occur with *m*-DMABN in acetonitrile and even to compensate for the small [1] decrease in the absolute value of the Coulomb energy  $C(A^-D^+)$  caused by the *meta*-position of the dimethylamino and benzonitrile ions in the hypothetical TICT structure of *m*-DMABN. Nevertheless, dual fluorescence is not observed for this molecule.

Another clearcut situation results when a second cyano group is added to *m*-DMABN, giving 3,4-dicyano-*N,N*-dimethylaniline (34-DCDMA). In this molecule, the energy of the proposed TICT state would be lowered (Eq. (1)) by an amount of 0.65 eV relative to that of DMABN, based on the difference between the reduction potentials of benzonitrile ( $-2.35$  V vs. SCE) and 1,2-dicyanobenzene ( $-1.70$  V vs. SCE) [6,7,9]. When the simultaneous decrease in energy ( $\sim 0.4$  eV) of the LE state of 34-DCDMA as compared to that of DMABN in acetonitrile is taken into account, an energy gain of around 0.25 eV relative to that of DMABN results for the ICT reaction [6] and efficient dual fluorescence should occur, which is not the case. A similar situation holds for 3,5-dicyano-*N,N*-dimethylaniline (35-DCDMA) [6,7].

### 3. Conclusions

The radiative rate constant  $k_f(\text{ICT})$  of dual fluorescent molecules such as DMABN is smaller than  $k_f(\text{LE})$  due to the larger admixture of CT (larger

dipole moment) in the ICT state. A conclusion on the validity of the TICT or PICT model can therefore not be drawn from these data. The absence of dual fluorescence for MABN, *m*-DMABN and two dicyano-*N,N*-dimethylanilines cannot be explained by the TICT hypothesis. It is caused by the fact that the requirement  $E(\text{ICT}) < E(\text{LE})$  cannot be fulfilled due to the large magnitude of  $\Delta E(S_1, S_2)$  in these molecules, see Fig. 1a.

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