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ADIABATIC PHOTOREACTIONS IN DILUTE SOLUTIONS OF *p*-SUBSTITUTED *N,N*-DIALKYLANILINES AND RELATED DONOR–ACCEPTOR COMPOUNDS*

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Summary

Twisted intramolecular charge transfer (TICT) stable excited states can occur in molecules in which two chromophores are separated by one (twisted) single bond. The TICT state is achieved by an adiabatic photoreaction after absorption to the lowest-lying Franck–Condon excited state of that molecule. This lower-lying TICT state potential minimum in the hypersurface of the lowest-lying excited state gives rise to the effect of dual fluorescence which allows us to study the kinetics of the twist mechanism. If the *para* substituent to the *N,N*-dialkylaniline is a large π electronic system (9-anthryl or sulphone) the aniline twists around that substituent, but if the substituent is small (nitrile or ester) the dialkylamino group twists around its phenyl ring. The population of the TICT state is favoured by (1) the dialkylamino group ionization potential, (2) the substituent electron affinity, (3) the lifetime of the excited state, (4) its dipole–dipole interaction with the solvent and (5) a low viscosity of the solution.

1. A naphthalene derivative

The discovery of the dual fluorescence of *p*-dimethylaminobenzonitrile (DMABN) by Lippert *et al.* [1] has since been a research topic of controversy. Grabowski *et al.* [2] have retained the original concept and have introduced the idea of two excited isomers differing in the orientation of the amino group relative to the aromatic plane.

This phenomenon of dual fluorescence also exists for 1-dimethylamino-4-cyanonaphthalene (DMANCN). Figure 1 shows a behaviour analogous to that of DMABN. At sufficiently low concentrations the observed fluorescence bands are not concentration dependent, ruling out dimer or excimer formation. Moreover, the similarity of the temperature dependence of the long-wavelength fluorescence F_A and short-wavelength fluorescence F_B quantum yields φ_A and φ_B to that for DMABN suggests the same mechanism, namely that of the formation of a highly polar twisted intramolecular charge transfer (TICT) state [3].

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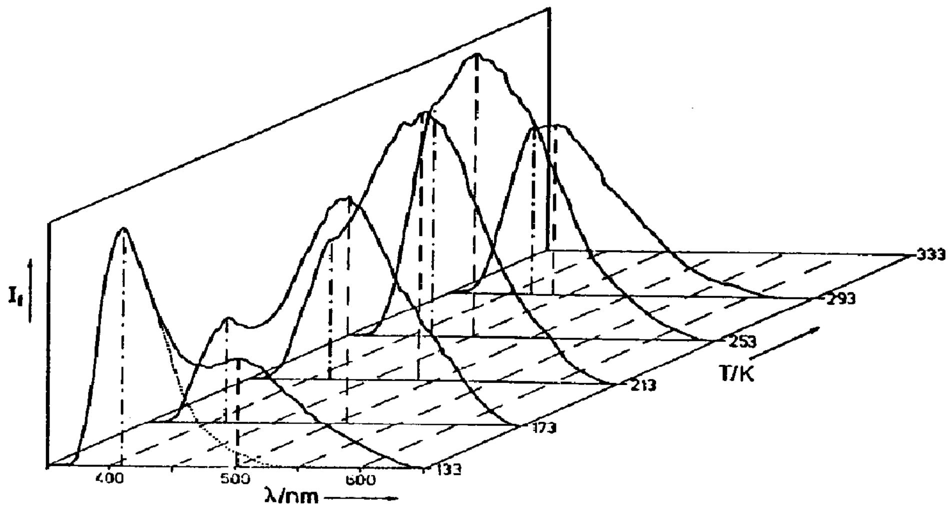

Fig. 1. The temperature dependence of the corrected fluorescence spectrum of DMANCN (3.7×10^{-6} M in *n*-butyl chloride) [3].

From the degree of polarization of the short-wavelength fluorescence band F_B as a function of temperature, an inversion of the ^1L_a and ^1L_b fluorescent states has been shown to occur in propylene glycol at room temperature [4]. This fluorescence level inversion is assumed to arise from reorientation effects of the solvent molecules. The long-wavelength fluorescence band F_A is emitted from a third state which is formed via an adiabatic photoreaction along a reaction coordinate involving solvent reorientation as well as solute geometrical relaxation (intramolecular twisting).

2. Adiabaticity

It has been shown recently [5] that, in contrast with DMABN, the TICT-forming twisting photoreaction occurs even in non-polar saturated hydrocarbon solvents for the *p*-diethylamino benzoic acid ethyl ester. It has been concluded from fluorescence polarization measurements [6] that the B* state for DMABN has ^1L_b symmetry, whereas the B* state for the ester and the TICT states for both compounds are polarized like ^1L_a. Thus the TICT formation process for the ester is a true adiabatic photoreaction in the Förster sense, whereas that for DMABN involves a transition between two hypersurfaces of different symmetries and is thus not truly adiabatic, although this term is also used in a more generalized way for describing photoreactions where the products finally arrive on an excited state surface irrespective of symmetry considerations [7].

The true adiabaticity for the ester is the key to the dual fluorescence in non-polar solvents. Measurements of the rate constant of TICT formation show it to be several times larger for the ester than for the corresponding nitrile. Thus for the nitrile the reaction is considerably slowed down by the necessity to cross from one state to another.

3. Sudden polarization

Recently *ab initio* calculations have been carried out for the simultaneous torsion and pyramidalization energy and dipole moment surfaces for the two lowest singlet excited states of ethylene (Fig. 2) [8].

Analogous results have been presented [9] concerning complete neglect of differential overlap–configuration interaction (CNDO/S–CI) calculations for DMABN (Fig. 2). The B* state and TICT state dipole moments differ remarkably, the latter moment being due to almost full charge separation. Although TICT formation involves twist around an essentially single bond and sudden polarization involves twist around an essentially double bond, it is seen that in both cases most of the charge separation occurs very close to the perpendicular geometry which is characterized by a very low exchange integral. In both cases the sudden polarization is linked to the fact that higher-lying states are lowered in energy by twisting.

4. Sulphones

TICT states are formed not only by simple donor–acceptor molecules. Molecules possessing two donor parts attached symmetrically to one acceptor moiety can show a multiple fluorescence originating partly from TICT states. For example, bis(4-*N*,*N*-dimethylaminophenyl)sulphone (DMAPS) shows an extremely broad fluorescence in ethanol, whereas its fluorescence band in hexane

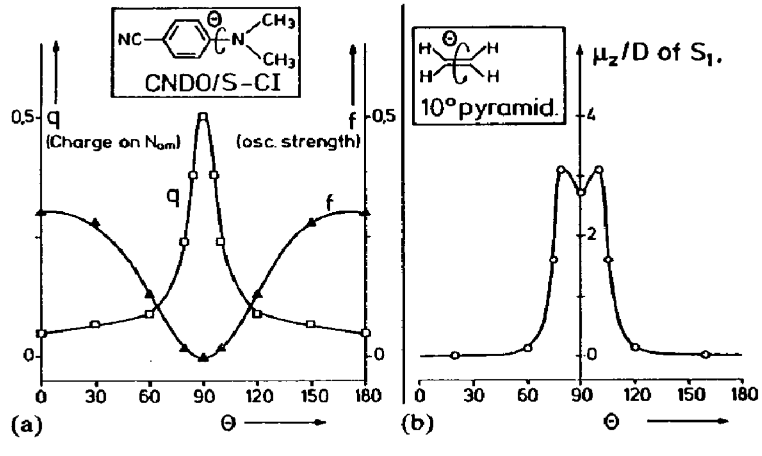

Fig. 2. Sudden polarization: (a) CNDO/S–CI calculations; (b) *ab initio* MRD–CI calculations (S_1 natural orbital basis) (from ref. 8).

is rather narrow ($\Delta\nu_{1/2} \approx 9000$ cm^{-1} in ethanol and $\Delta\nu_{1/2} \approx 3000$ cm^{-1} in hexane).

If the ethanol spectra are deconvoluted, assuming the hexane fluorescence band shape for the short-wavelength fluorescence band F_B, the quantum yields of long-wavelength (φ_A) and normal (φ_B) fluorescence can be calculated as well as their ratio. The result is that their temperature dependence is quite similiar to that for DMABN, and this is indicative of an excited state equilibrium between two species $B^* \rightleftarrows A^*$. From the concentration and excitation energy independence, intermolecular mechanisms may be ruled out and the phenomenon is best explained by TICT state formation as for DMABN.

For DMAPS, two possibilities of intramolecular rotation to form a TICT state exist: (1) around the phenyl–amino bond as in DMABN; (2) around the phenyl–SO_2 bond. This question can be answered by considering Fig. 3 which shows the fluorescence spectra of bis(4-aminophenyl)sulphone (APS) in moderately and strongly polar solvents: the spectra are very similar to those of DMAPS.

In this case, one of the internal rotations (that around the phenyl–amino bond) can be ruled out because the isolated NH_2 substituent is not a good enough donor (easily verified experimentally by inspecting the (dual) fluorescence spectra of amino, *N*-methylamino and *N*,*N*-dimethylamino benzenes with an acceptor substituent in the *para* position that is stronger than that in APS). Thus, from the occurrence of dual fluorescence in APS, it is concluded that the TICT state is formed by rotation of one benzene nucleus (plus substituent) around the phenyl–SO_2 bond.

It is probable that numerous analogous cases to APS and DMAPS exist where rapid deactivation of the initially formed excited state can be achieved through internal rotation towards a fluorescent or a non-fluorescent TICT state. Michler's ketone (bis(4-dimethylaminophenyl)ketone), for example, is known

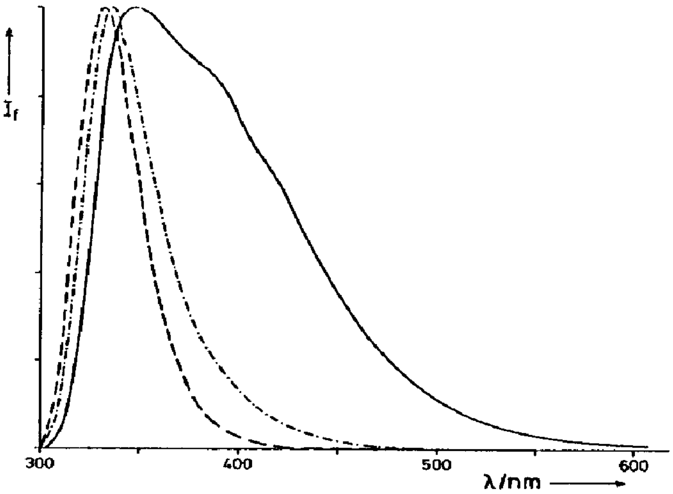

Fig. 3. Corrected fluorescence spectra (room temperature) of dilute solutions of APS in aprotic solvents of different molecular size and polarity: – – –, *n*-butyl chloride; – • – •, dichloromethane; ——, acetonitrile.

to have a very weak and extremely short-lived fluorescence at room temperature [10] which could be explained by rapid TICT state formation ($>C=O$ is a stronger acceptor than $>SO_2$).

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