

## Molecule Matters

### 4-(N,N-dimethylamino)benzonitrile: A Twist in the Excited State?

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**4-(N,N-dimethylamino)benzonitrile, popularly known as DMABN, has received tremendous attention for nearly five decades. In this article, we outline some of the features of the molecule that have made it such an interesting system to study, such as fluorescence emission in two wavelengths. The article also highlights how limited our understanding of the excited state structure of a small molecule like DMABN is, despite the availability of various resources to investigate it.**

If one can judge a molecule by its chemical formula then 4-(N,N-dimethylamino)benzonitrile (DMABN) should be termed as a simple, innocuous molecular system. Certainly, it does not look like a molecule that is exciting. However, the molecule has captured the attention of many for the past 45 years [1] and it is quite likely that it will continue to receive a great deal of attention for some more time to come. While this article is devoted to the most discussed and debated aspect of DMABN, readers should note its potential application as a reporter molecule for probing the microenvironments of various organized assemblies, sensor for metal ions, and a model system for the understanding of photo-induced charge separation process, including photo-synthesis.

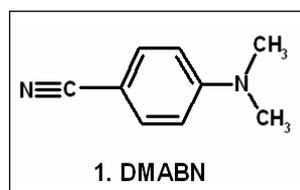
Excitation of aromatic organic molecules by light of a particular wavelength often leads to emission of light of higher wavelength (lower energy); this is the well-known phenomenon of fluorescence. Fluorescence usually originates from the lowest excited electronic state (singlet) irrespective of the excitation and hence, the fluorescence spectrum of a molecule is characterized by a single band. However, what makes DMABN a very special molecule is that it exhibits dual fluorescence (i.e. emission of

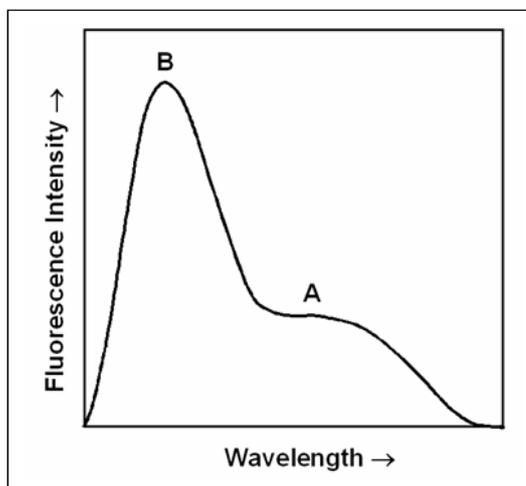


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#### Keywords

Dual fluorescence, TICT.





**Figure 1.** A pictorial illustration of dual fluorescence of DMABN.

light having two colors), as discovered by Lippert in 1961 [2]. A large majority of studies on this and related systems is aimed at finding out why DMABN exhibits two fluorescence bands, whereas most other systems exhibit only one.

A clue to answer this question can be found if one studies the effect of solvent polarity on the fluorescence behaviour of DMABN [2]. One of the two emission bands that appears in the short-wavelength region (termed as ‘normal’ or ‘B-fluorescence’) is somewhat insensitive to

the polarity of the medium. In contrast, the long-wavelength fluorescence band (described as ‘anomalous’ or ‘A-fluorescence’) is remarkably sensitive to solvent polarity. An increase in the polarity of the medium leads to a drastic shift of the maximum of the band towards the longer wavelength. These simple experiments suggest that the anomalous A-fluorescence originates from a state that is highly polar and hence influenced very strongly by the polarity of the solvent. A quantitative study of the solvent effect on the absorption and emission yielded a dipole moment of 23 D for this state [2].

One of the early postulates made to explain the dual fluorescence of DMABN was the ‘State Reversal’ or ‘B→A inversion’ model. According to this simple model, DMABN has two close-lying excited states, indicated here as A and B states. In nonpolar media, the less polar ‘B-state’ is the lowest excited state from which the fluorescence originates. However, in polar media, stabilization of the highly polar ‘A-state’ brings it below the ‘B-state’ making it the lowest state [3].

The most popular explanation for the dual fluorescence of DMABN is the twisted intramolecular charge transfer (TICT) mechanism.

Some alternative mechanisms were proposed later to account for the dual fluorescence of DMABN [1]. However, since none of these postulates stood the test of time, we will skip them and move to the well-known, but controversial, Twisted Intramolecular Charge Transfer (TICT) mechanism. According to this



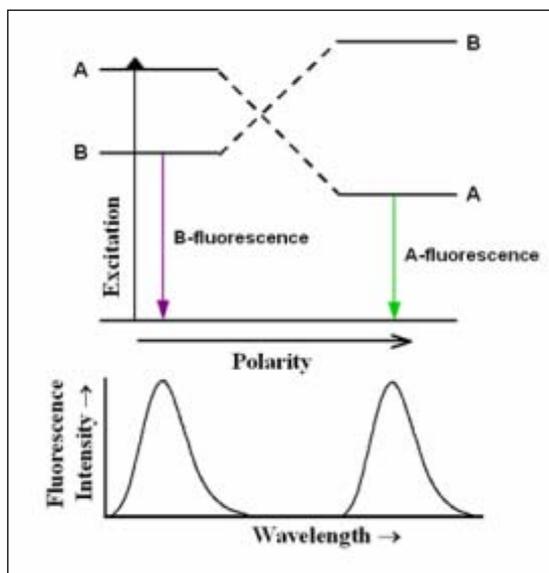


Figure 2. The 'State Reversal' model.

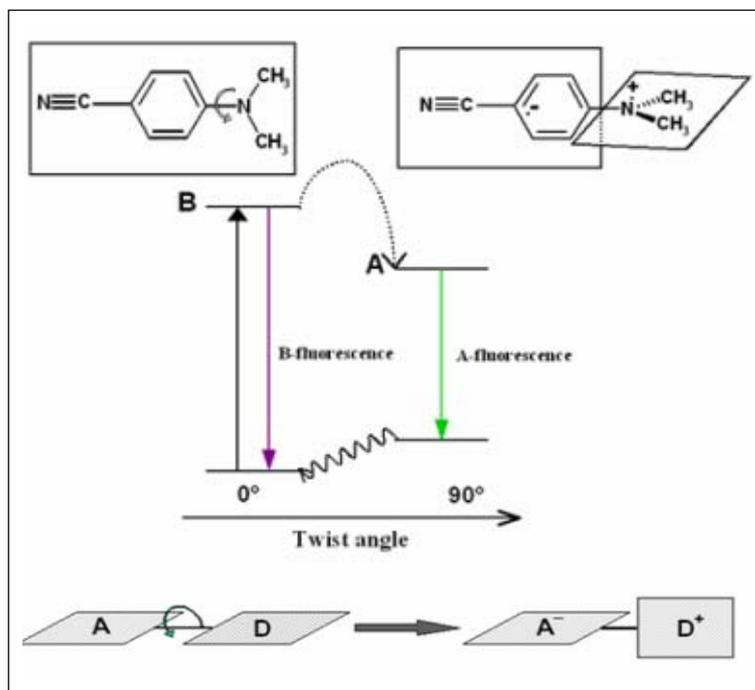
mechanism, proposed by Grabowski and coworkers [4] almost 11 years after Lippert's discovery [2], the B-fluorescence arises from a coplanar structure of DMABN, whereas the A-fluorescence originates from a structure in which the dimethylamino ( $\text{NMe}_2$ ) group is twisted  $90^\circ$  with respect to the cyanophenyl moiety. The high dipole moment associated with this structure is attributed to the transfer of one electron from the electron rich  $\text{NMe}_2$  donor group (D) to the electronically deficient cyanophenyl acceptor (A) group. In essence, according to the TICT model, photoexcitation of DMABN leads to structural change (twisting) accompanied by transfer of one unit of charge from one part of the molecule to another. The reader should make a clear distinction between the State Reversal model and the TICT model by noting the fact that the former model does not involve any change in the molecular structure, whereas the concept of structural change is key to the TICT mechanism.

It is perhaps important to highlight here what necessitated a model involving structural change of the molecule. This can be understood if one recognizes the experimental observations with a family of related molecules: **2** exhibits both A- and B-fluorescence; **3**, which cannot assume a planar conformation because of

In TICT mechanism, 'B-fluorescence' is from the excited state of DMABN having a planar geometry while 'A-fluorescence' is from a state with a twisted geometry.

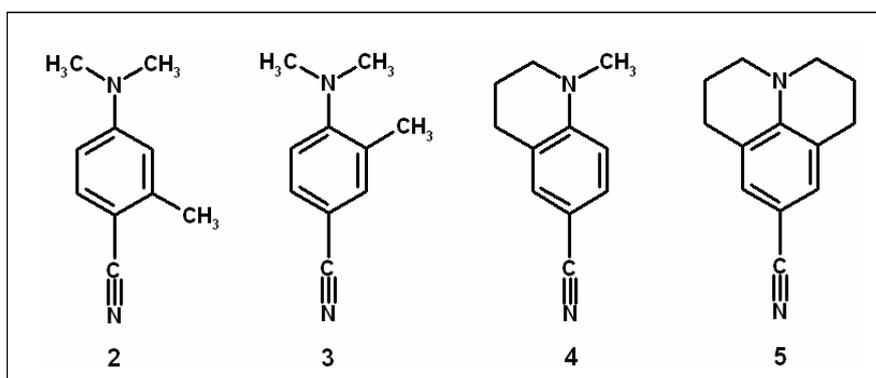


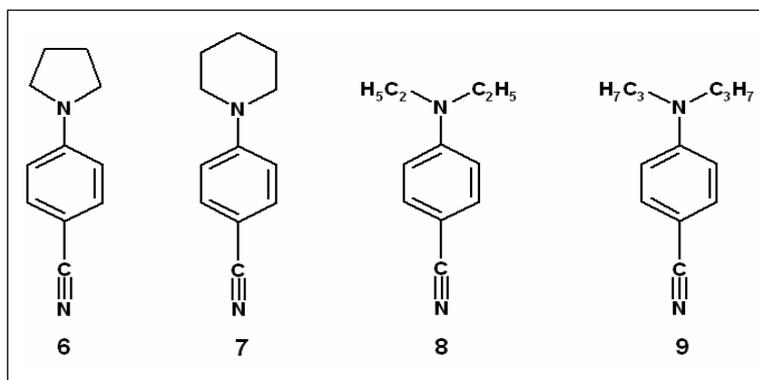
Figure 3. The TICT model.



steric repulsion with the methyl group in the *ortho* position, shows almost exclusively A-fluorescence; **4** and **5**, which cannot assume a twisted structure, exhibit only the B-fluorescence [1].

The TICT mechanism was very well received as it explained most of the experimental data on DMABN derivatives and other systems of this type [5]. However, as there was no direct structural evidence to support the TICT mechanism, this model has been questioned time and again and alternative mechanisms have been



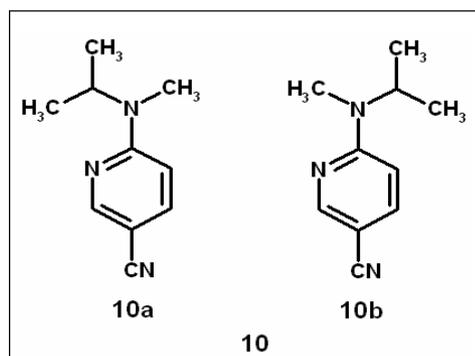


TICT explains most of the experimental data, but there have been objections to it. The other models have their own drawbacks and none of them is as favored as the TICT model.

proposed, particularly since 1992 [6,7,8]. Some of the weaknesses of the TICT model that led to the emergence of alternative ideas can be appreciated if one considers systems **6** and **7**. According to the TICT model, **6** should exhibit more A-fluorescence compared to **7** as it contains a smaller group that needs to be rotated in the twisting process. However, the opposite is observed experimentally. The same is the case with **8** and **9**. The latter having a bulkier amino moiety exhibits more A-fluorescence compared to **8**, again in disagreement with the TICT model. Among the alternative models, pyramidalization around the amino nitrogen (WICT) [6], cyano-bending (RICT) [7] and planarization around the amino nitrogen (PICT) [8] are noteworthy (*Box 1*). However, each model has its drawback and none of these models can be considered seriously as a substitute for the TICT model.

This short account on DMABN will be incomplete if it does not refer to a work, which certified that the TICT model passed a critical test [9]. **10** is a DMABN analogue that exhibits dual fluorescence. A-fluorescence of **10** was found to be accompanied by *syn-anti* (**10a**–**10b**) photoisomerisation, which implies twisting around the C-N bond in the excited state vindicating the TICT model.

How does one resolve the dilemma? The issue here is to find out the structure of a molecule in the excited state. One can determine the structure of a



**Box 1. Alternative Models: Essential Ideas**

- WICT model: Photo-excitation leads to pyramidalization of the amino nitrogen.  
PICT model: Photo-excitation leads to planarization of the amino nitrogen.  
RICT model: Photo-excitation leads to bending of the cyano group.

molecular system accurately by X-ray diffraction study of its single crystal. Is it not possible then to determine the excited state structure of DMABN using this technique? Attempts have indeed been made to determine the structure of DMABN and/or a related molecule while it is in the excited A-state [10]. In this experiment, one uses a short laser pulse to prepare the molecule in the desired excited state and then performs the diffraction measurements. However, unlike the ground state measurement, this experiment is extremely difficult as the molecule stays in the excited state only for a very short period (typically a few nanoseconds). Further, the restrictions on molecular geometry changes are quite severe in the crystalline state. It is primarily due to these limitations that the excited state X-ray diffraction studies on DMABN related systems have not yielded results that are convincing.

The structural information on molecular systems, in particular the bond length, is also frequently obtained from infrared or resonance Raman spectroscopic measurements. Is it not possible to carry out these measurements while DMABN is in the A-state and determine whether the C-N bond is more like a single bond (if the TICT model is correct) or like a double bond (if PICT model is correct)? Unfortunately, results of different experiments performed on DMABN are contradictory and no unambiguous conclusion could be drawn so far [11]. A large number of theoretical calculations, including highly sophisticated ones, have been performed on DMABN and its derivatives to resolve the twist or no-twist issue [1]. While the results largely support the TICT mechanism, one cannot rule out the other models completely. It thus turns out that despite the availability of various sophisticated experimental techniques and extensive computational facilities, it is still not possible to determine accurately the excited state

Unfortunately, results of different experiments performed on DMABN are contradictory and no definite conclusion is available yet, though the results are largely in favor of the TICT mechanism.



structure of a simple molecule such as DMABN. Therefore, the debate on the TICT mechanism still continues.

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