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# An Experimental Test of C−N Bond Twisting in the TICT State: Syn−Anti Photoisomerization in 2-(*N*-Methyl-*N*-isopropylamino)-5-cyanopyridine

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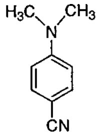
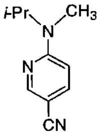
A previously untested essential consequence of the twisted internal charge transfer (TICT) interpretation of the nature of the "anomalous" excited state of *p*-dimethylaminobenzonitrile (**1**) and related compounds has now been verified: at −90 °C, the dual fluorescence of a desymmetrized analogue, 2-(*N*-methyl-*N*-isopropylamino)-5-cyanopyridine (**2**) in methanol (MeOH) is accompanied by syn−anti isomerization around the C−N bond, whereas its ordinary fluorescence in tetrahydrofuran (THF) is not.

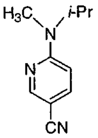
Lippert's 1962 observation[2] of dual fluorescence from **1** in polar solvents and subsequent reports of similar behavior for many related compounds, including aza heterocycles, have presented molecular photophysics with a puzzle that has eluded a satisfactory solution.



**1**



**2a**



**2b**

The assignment of the ordinary emission ($F_b$) to an approximately vertically excited $L_b$ state has never been questioned, but after hundreds of publications, the nature of the geometrical distortion that leads to the polar excited state responsible for the strongly red-shifted anomalous emission ($F_a$) with a small radiative constant is still in dispute. The common TICT acronym for this state reflects the structural interpretation proposed by Grabowski et al.,[3] in which the amino group of the relaxed emitting state is twisted ~90° to the aromatic plane, planarized,[4] and positively charged, while a negative charge is delocalized over the rest of the molecule. Theoretical arguments[5,6a] as well as numerical computations[7,8] support the notion that the excited charge-transfer (CT) state of a $\pi$-linked donor−acceptor pair stabilizes by twisting, and the concept has been used to interpret photophysical properties of neutral donor−acceptor molecules and donor−acceptor cations such as triphenylmethane and cyanine dyes.[9] In the TICT model, the small barrier separating the vertical and twisted emissive states results from their avoided crossing along the twisting coordinate.[6b] The vertical upper excited state is mostly $L_a$ and it drops in energy and acquires increasing CT character with increasing twist, while the lower $L_b$ state rises. Theory suggests that near ~90° the lowest CT singlet and triplet are very close in energy (small exchange integral between the donor and acceptor orbitals); intersystem crossing from the anomalous emissive state into the triplet manifold seems facile.[10]

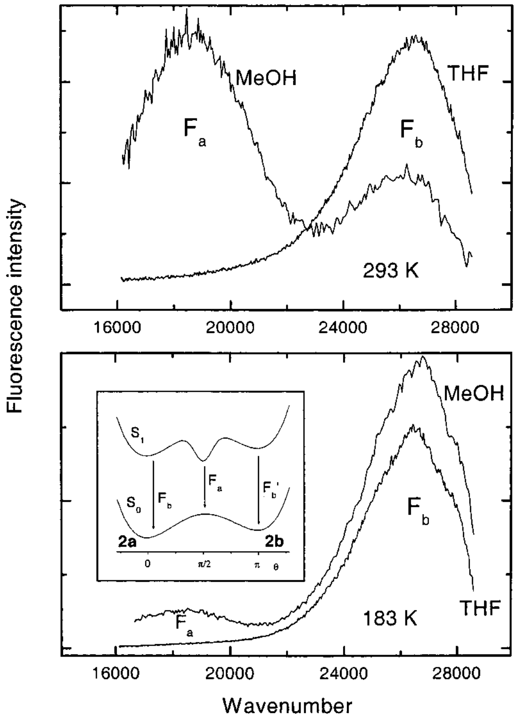


***Figure 1.*** Anomalous ($F_a$) and ordinary ($F_b \approx F_b'$) fluorescence of **2** in MeOH and in THF at 293 and 183 K. Inset (TICT model): schematic $S_0$ and $S_1$ energies of **2** as a function of the C−N twisting coordinate $\theta$.

Although TICT is the most commonly accepted structure for the anomalous emissive state, there is no direct evidence for it, and it is being vigorously challenged.[11,12] Alternative assignments attribute $F_a$ to an exciplex[13] or, more often, to a structural distortion other than twisting,[14,15] but any evidence for them is also only indirect. This situation contrasts starkly with that in alkenes, for which similar simple theoretical arguments apply,[5] and whose excited states are shorter lived, nonemissive, and much harder to observe directly. Yet, since electronic excitation of alkenes leads to cis−trans isomerization while preserving the integrity of all single bonds,[16] it is generally accepted that regardless of which other motions it involves, it must also involve twisting.

If the TICT interpretation is correct, $F_a$ must also be accompanied by syn−anti isomerization around the C−N bond. Conversely, if the isomerization did occur under conditions in which $F_a$ is observed and failed to occur under conditions in which only $F_b$ appears, the likelihood that the TICT assignment is correct would increase considerably.[17] The molecule again keeps its integrity, and the photoisomerization path would have to involve C−N bond twisting

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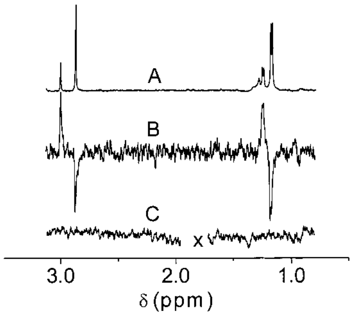

***Figure 2.*** $^1$H NMR of **2** (183 K): spectrum in MeOH (A), and light-dark difference spectra in MeOH (B) and in THF (C). The crossed-out region is blocked by the solvent.

in the excited state close to or even past orthogonality at some point after passing the small barrier separating the anomalous emissive state from the initial vertical geometry. This would only be possible if (i) the anomalous emissive state were itself twisted, TICT (Figure 1, inset), or if (ii) it were distorted in some other way that opened previously denied access to yet another intermediate excited-state minimum or funnel at a twisted geometry before the final formation of an isomerized ground-state product. In the absence of any experimental or computational evidence for additional twisted states other than the anomalous emissive singlet and the corresponding triplet,[18] Occam's razor would favor the TICT model.

Any attempt to find out whether $F_a$ is accompanied by syn−anti isomerization is complicated by the only partial double character of the C−N bond in the ground state, leading to a low syn−anti isomerization barrier of $\sim$10−20 kcal/mol,[19] and rapid thermal syn−anti equilibration. Low temperatures must be used with caution, lest the excited state barrier separating the initial vertically excited state from the anomalous emissive state should become prohibitive. We find that the use of **2** in MeOH and THF at $\sim$−90 °C is a suitable compromise. The photophysical characteristics, and particularly, the fluorescence emissions of **2** (Figure 1) are very similar to those of **1**, but the syn (**2a**) and anti (**2b**) conformers have distinct NMR spectra. The structural assignment was secured by low-temperature $^1$H NOE of **2** in MeOH, which leaves no doubt that **2a** and **2b** are geometrical isomers, irrespective of other ways in which they might also differ, such as hydrogen bonding to the solvent.

Photoinduced geometrical isomerization was detected as difference $^1$H NMR (Varian UNITY500+, 500.6 MHz, 1800 cycles averaged). In each cycle a single 308 nm excimer laser pulse was absorbed by a solution of **2**, a spectrum was collected after a small known delay, and a spectrum collected under identical conditions but in the dark was subtracted (equilibrium is reestablished in less than 1 s). In MeOH at −90 °C, where both $F_a$ and $F_b$ are seen (Figure 1), the NMR difference spectrum (Figure 2) shows photodepletion of **2a** and photoenrichment of **2b**. The results at −70 to −90 °C are similar and prove that **2** photochemically syn−anti isomerizes. In pure THF at −90 °C, $F_b$ is strong but $F_a$ is inobservably weak, as is syn−anti isomerization. In MeOH−THF mixtures, the $F_a/F_b$ intensity ratio and the NMR difference intensity are correlated; % MeOH, $I(F_a)/I(F_b)$, $I_{NMR}$: 0, 0, 0; 10, 0.020, 0; 20, 0.39, 0.15; 30, 0.036, 0.18; 50, 0.055, 0.18; 75, 0.066, 0.22; 100, 0.105, 1. A symmetrically N-substituted molecule, 2-(*N*,*N*-diethylamino)-5-cyanopyridine, gives no NMR difference signal.

The TICT model of Grabowski et al.[3] has passed a critical test.

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(1) 2-Chloro-5-cyanopyridine was refluxed in dioxane with 4 equiv. of methylisopropylamine for 12 h. The solvent was evaporated; the residue was dissolved in a small amount of water, rendered alkaline with NaOH, and extracted with ether. The ether solution was dried with $MgSO_4$ and evaporated. The residue was crystallized from isopentane at 283 K, yielding colorless crystals of **2**, mp 53−54 °C. Yield, 60%. $^1$H NMR ($CDCl_3$) $\delta$ 1.15 (d, $J = 6.3$ Hz, 6H, $CHCH_3$); 2.80 (s, 3H, $NCH_3$); 4.80 (septet, $J = 6.3$ Hz, 1H, $CHCH_3$); 6.25 (d, $J = 8.8$ Hz, 1H, $H^3$); 7.35 (dd, $J = 8.8$ Hz, 2.0 Hz, 1H, $H^4$); 8.12 (d, $J = 2.0$ Hz, 1H, $H^6$); $^{13}$C NMR ($CDCl_3$) $\delta$159.1, 152.5, 139.3, 119.0, 105.3, 94.9, 45.9, 28.5, 19.4; IR (KBr) 2209, 1602, 1538, 1505, 1454, 1403, 1393, 1314, 1207, 1128, 811 cm$^{-1}$; UV (hexane) $\lambda_{max} = 279$ nm, $\epsilon_{max} = 31\,000$; MS (EI) *m/z* (rel intens) 175 (22), 161 (11), 160 (100), 132 (15), 119 (16), 103 (14). Anal. Calcd for $C_{10}N_3H_{13}$: C, 68.54; H, 7.48; N, 23.98. Found: C, 68.45; H 7.48; N 24.16.

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(17) Since the anomalous emissive state is at an energy comparable to that of the ordinary one, one can hardly postulate a hot-ground-state twisting mechanism for the former but not the latter.

(18) The lowest triplet charge-transfer state is the only obvious candidate for an additional twisted state. Even if one were to disregard theoretical arguments and claim that the singlet anomalous emissive state is distorted otherwise but its triplet analogue is twisted, and that the isomerization reaction proceeds from the former to the latter (triplet TICT path), it would not be apparent why the latter could not be reached just as well from the initial vertically excited singlet state which is known to undergo intersystem crossing: Koehler, G.; Grabner, G.; Rotkiewicz, K. *Chem. Phys.* **1993**, *175*, 295. Rotkiewicz, K.; Herbich, J.; Peres-Salgado, F.; Rettig, W. *Proc. Ind. Acad. Sci. (Chem. Sci.)* **1992**, *104*, 105.

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