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 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.

The assignment of the ordinary emission (Fb) to an approximately vertically excited Lb 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 (Fa) with a small radiative constant is still in dispute. The common TICT acronym for this state reflects an excitation leading to the polar excited state responsible for the strongly red-shifted anomalous emission (Fa) with a small radiative constant, but a negative charge is delocalized over the rest of the molecule.

Theoretical arguments5,6a as well as numerical computations7,8 support the notion that the excited charge-transfer (CT) state of a π-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.9b The vertical upper excited state is mostly Lb and it drops in energy and acquires increasing CT character with increasing twist, while the lower Lb 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

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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 Fa to an exciplex13 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,3 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, Fa must also be accompanied by syn–anti isomerization around the C–N bond. Conversely, if the isomerization did occur under conditions in which Fa is observed and failed to occur under conditions in which only Fb 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.

Figure 1. Anomalous (Fa) and ordinary (Fb = Fb′) fluorescence of 2 in MeOH and in THF at 293 and 183 K. Inset (TICT model): schematic S0 and S1 energies of 2 as a function of the C–N twisting coordinate θ.

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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 intermediates geometry. The results at 90 °C 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 1H 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.

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

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References

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 MgSO4 and evaporated. The residue was crystallized from isopentane at 283 K, yielding colorless crystals of 2, mp 53–54 °C. Yield, 60%. 1H NMR (CDCl3) δ 1.15 (d, J = 6.3 Hz, 6H, CH2CH3); 2.65 (d, J = 8.8 Hz, 4H); 7.35 (dd, J = 8.8 Hz, 2H, H2); 8.12 (d, J = 2.0 Hz, 1H, H4); 11.25 (s, 1H, N).

2. Figure 2. 1H 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 yielding colorless crystals of 2, mp 53–54 °C. Yield, 60%. 1H NMR (CDCl3) δ 1.15 (d, J = 6.3 Hz, 6H, CH2CH3); 2.65 (d, J = 8.8 Hz, 4H); 7.35 (dd, J = 8.8 Hz, 2H, H2); 8.12 (d, J = 2.0 Hz, 1H, H4); 11.25 (s, 1H, N).

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