Supporting Information for:

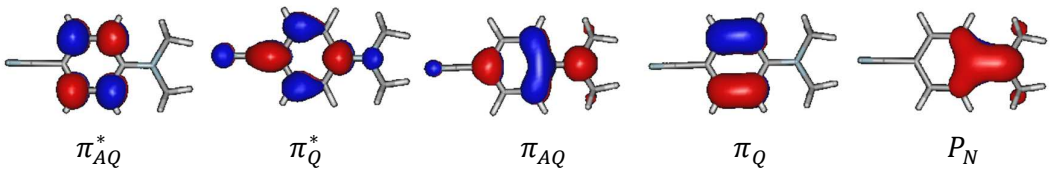
Insight into the Mechanisms of Luminescence of Aminobenzonitrile and Dimethylaminobenzonitrile in Polar Solvents. An Ab Initio Study

Isabel Gómez, Pedro J. Castro and Mar Reguero[*]

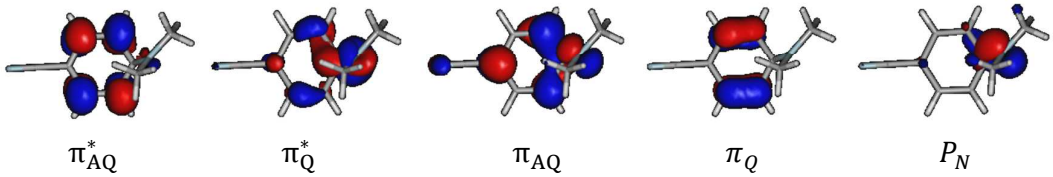
Departament de Química Física i Inorgànica.
Universitat Rovira i Virgili. Marcel.lí Domingo 1, 43007, Tarragona (Spain).

Figure S1. Molecular orbitals and excitations that describe the lowest excited states of DMABN on selected critical points. "Q" and "AQ" stand for "quinoidal" and "antiquinoidal".

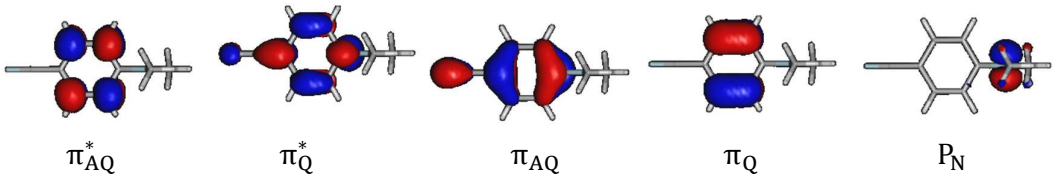
FC, LE and PICT:



TS(LE→TICT):



TICT:



$$LE(S_1) = {}^1\left(\pi_{AQ} \rightarrow \pi^*_{AQ}\right) + {}^1\left(\pi_Q \rightarrow \pi^*_Q\right)$$

$$PICT(S_2) = {}^1\left(\pi_{AQ} \rightarrow \pi^*_Q\right)$$

$$TICT(S_1) = {}^1\left(P_N \rightarrow \pi^*_Q\right)$$

Figure S2. Geometries of the ground-state, LE, PICT, RICT and TICT minima, and the transition state connecting LE and TICT species, optimized in the gas phase for ABN and DMABN. All bond lengths are in Å.

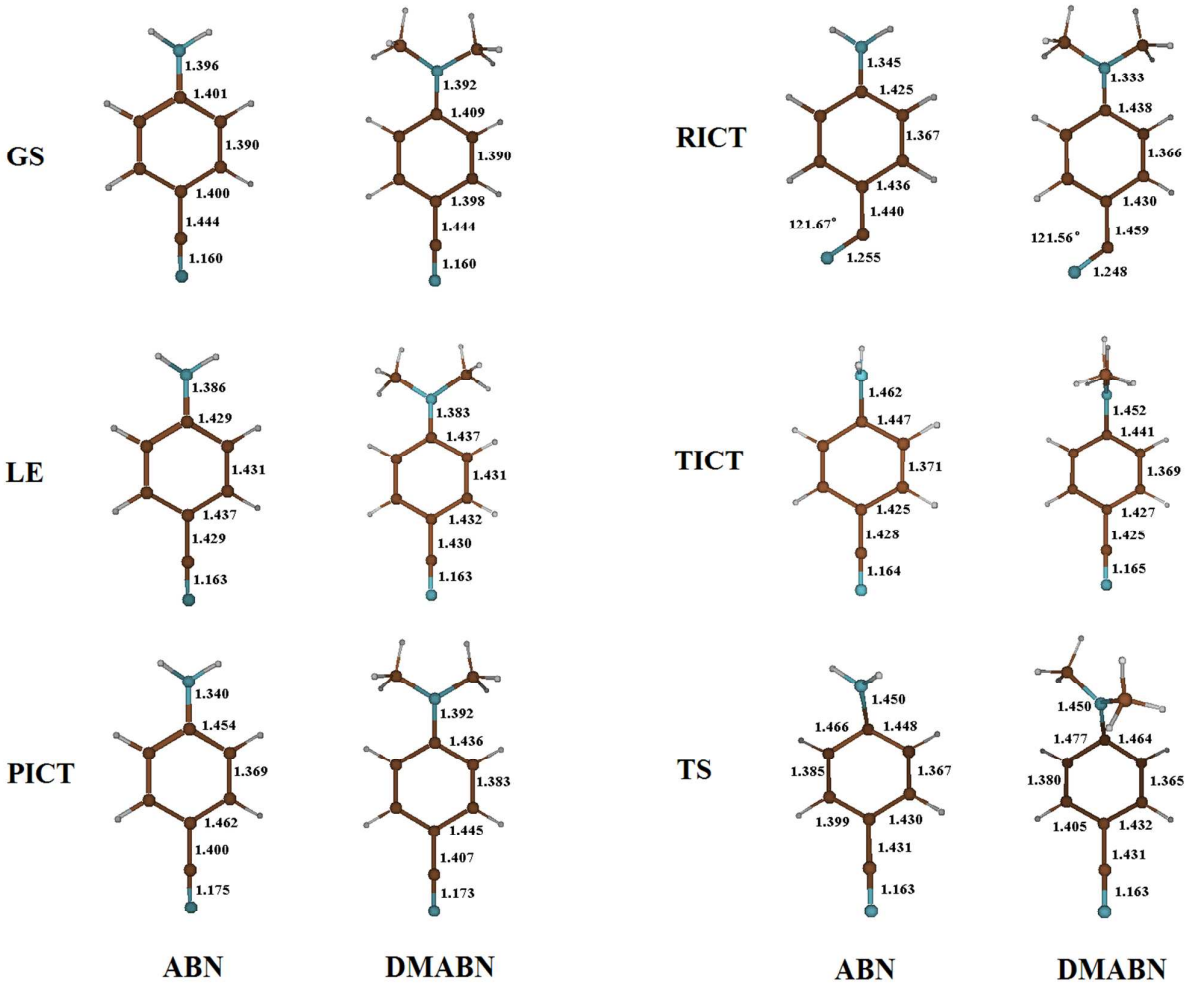


Figure S3. Geometries of the ground-state, LE, PICT, RICT and TICT minima, and the transition state connecting LE and TICT species, optimized in acetonitrile for ABN and DMABN. All bond lengths are in Å.

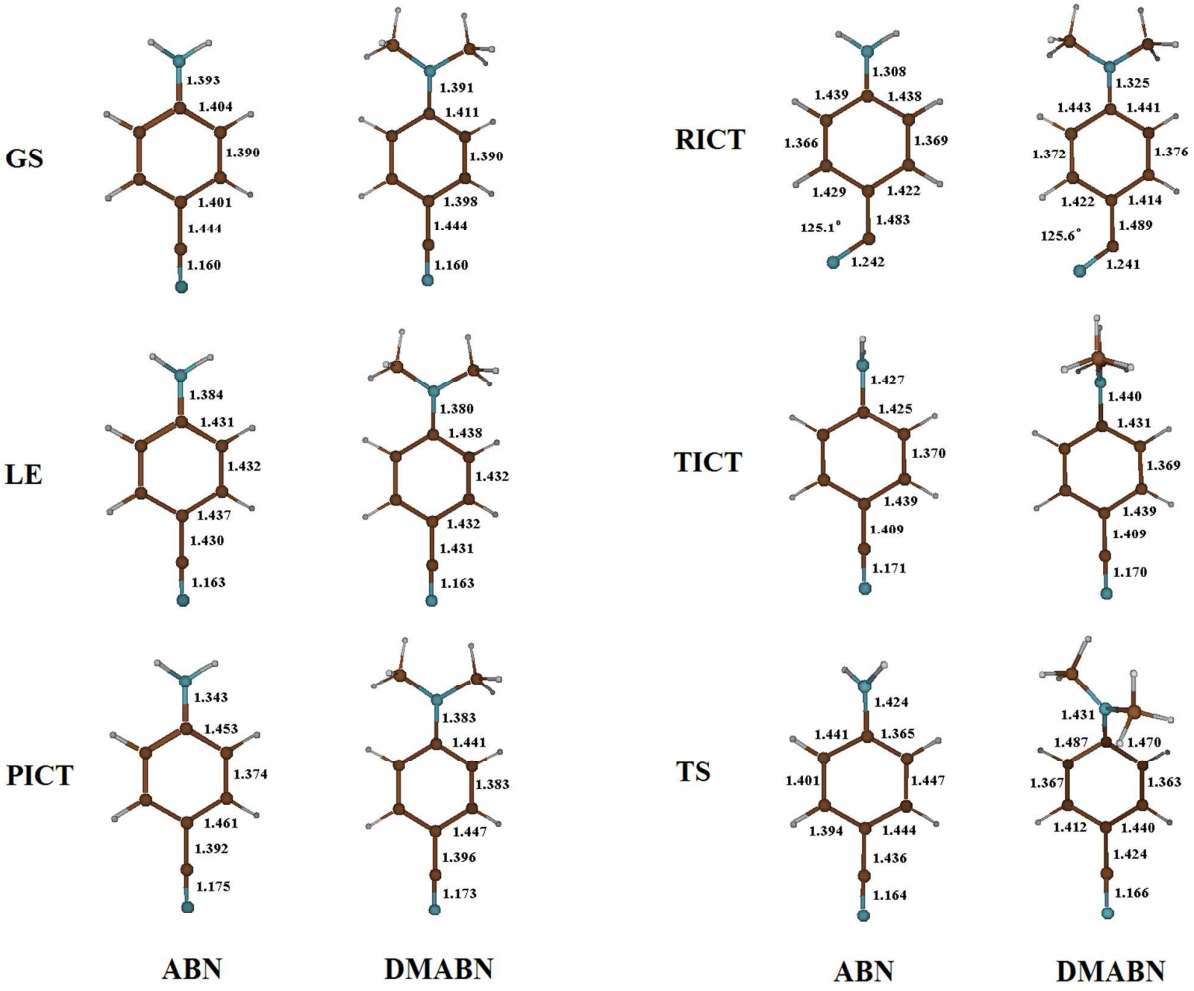


Figure S4. Forces in the potential energy surface of the S_2 (CT) state calculated at the CASSCF(12,11)/6-31G(d) level in Franck-Condon region of DMABN.

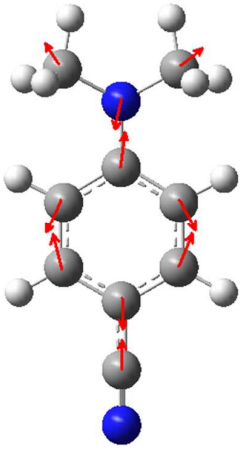
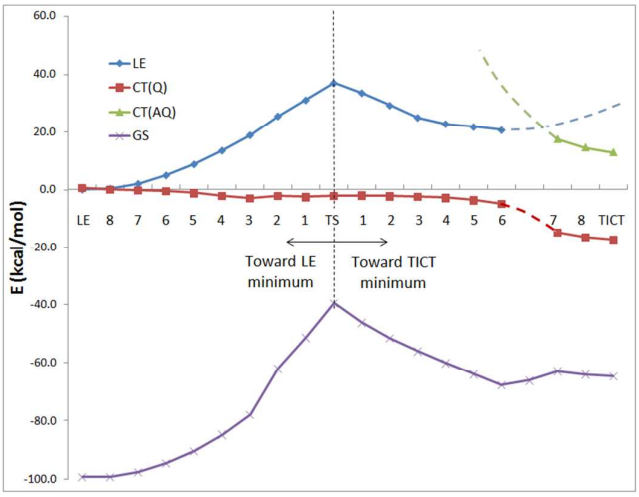


Figure S5. Energy profiles of the S_0, S_1 and S_2 PES from the TS that connects the LE and TICT minima, and each one of these minima. The profiles were obtained by a linear interpolated internal reaction coordinate path at the SA3-CASSCF(12,11)/CASPT2/cc-pVDZ level in acetonitrile. All energies are in kcal mol^{-1}, relative to the LE minimum.

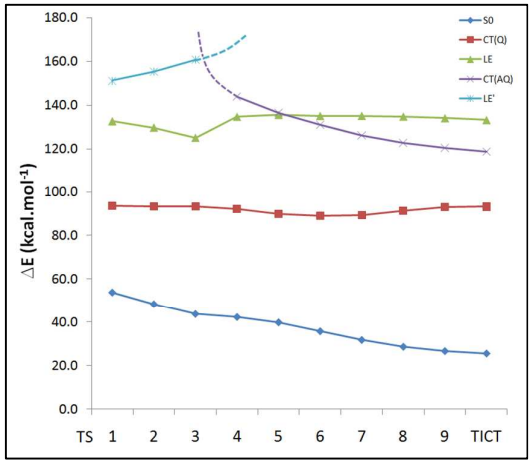
Point in the path	ΔE CASPT2 LE	ΔE CASPT2 CT(Q)	ΔE CASPT2 CT(AQ)
S_1-LE	0.0	0.6	-
8	0.3	0.1	-
7	2.0	-0.2	-
6	4.9	-0.5	-
5	8.7	-1.2	-
4	13.5	-2.2	-
3	18.8	-3.0	-
2	25.4	-2.2	-
1	31.0	-2.6	-
S_1-TS	36.9	-2.1	-
1	33.5	-2.0	-
2	29.2	-2.2	-
3	24.9	-2.5	-
4	22.7	-2.8	-
5	21.7	-3.7	-
6	20.6	-4.9	-
7	-	-14.9	17.4
8	-	-16.5	14.6
S_1-TICT		-17.3	12.9



Stability of the results of the profiles of Figure 3 with the average of states.

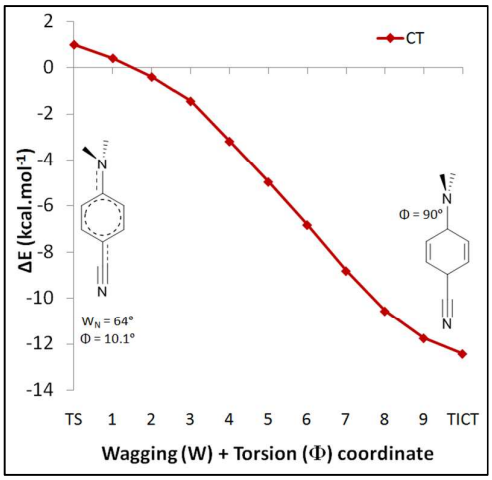
The conditions of the state average (SA) have an influence in the results. As the number of states averaged increases, the description of each state deteriorates at the CASSCF level. At the CASPT2 level, the better the reference function, the better the results in the perturbation calculations. So with larger state averages, the CASSCF as well as the CASPT2 results are less accurate.
Obviously, the best option is to perform calculations without state average, but it can lead, in some cases, to convergence problems impossible to resolve. This was the case here, given the crossings of states present in these profiles. In Figure 3 we have used a SA-3 to calculate at the same time the profiles of states S_0, S_1 and S_2.
To include both LE and CT(AQ) to avoid the discontinuity in point-7, we repeated the calculation with a SA-4, but the energy of the CT(AQ) state increases very quickly when approaching the TS, producing another crossing, so the states involved in the average change again, producing another discontinuity (Figure S6).

Figure S6. Energy profiles of the S_0, S_1 and S_2 PES from the TS to the TICT minimum. The profiles were obtained by a linear interpolated internal reaction coordinate path at the SA4-CASSCF(12,11)/CASPT2/cc-pVDZ level in acetonitrile. All energies are in kcal mol^{-1}, relative to the ground state minimum.



On top of this, the inclusion of the fourth state modifies noticeably the profile of the S_1-CT state, where a minimum at partially rotated geometries appears. Given the controversy about the existence of this pTICT minimum, we tried to recalculate the CT profile in the most accurate way (within our methodology), i. e., without state average. Unfortunately these calculations did not converged at every point, so SA-2 was used instead, with weights of 90% for CT and 10% for S_0. The profile obtained, show in Figure S7, show a monotonous decrease until the TICT geometry (torsion angle =90º), discarding the existence of a stable pTICT species in this system.

Figure S7. Energy profile of the S_1–CT surface from the TS to the TICT minimum for DMABN in acetonitrile. The profile was obtained by a linear interpolated internal reaction coordinate path at the CASSCF(12,11)/CASPT2/cc-pVDZ level with a SA2 and weights of 90% fot the CT state and 10% of the ground state. All energies are in kcal mol^{-1}, relative to the LE minimum.



Complementary references

TICT model:

- Rettig, W.; Bliss, B.; Dirnberger, K. Pseudo-Jahn-Teller and TICT-models: A Photophysical Comparison of meta- and para-DMABN Derivatives. *Chem. Phys. Lett*. **1999**, *305*, 8.
- Rettig, W. In *Topics in Current Chemistry, Electron-Transfer I*; Mattay, J., Ed.; Springer: Berlin, 1994; Vol. 169, pp 253-299.

WICT model:

- Leinhos, U.; Kühnle, W.; Zachariasse, K. A. Intramolecular Charge Transfer and thermal Exciplex Dissociation with p-Aminobenzonitriles in Toluene. *J. Phys. Chem*. **1991**, *95*, 2013-2021.

General analysis of different models:

- Dreyer, J.; Kummrow, A. Shedding Light on Excited-State Structures by Theoretical Analysis of Femtosecond Transient Infrared Spectra: Intramolecular Charge Transfer in 4-(Dimethylamino)benzonitrile. *J. Am. Chem. Soc*. **2000**, *122*, 2577-2585.

π–σ* state:

- Lee, J. K.; Fujiwara, T.; Kofron, W. G.; Zgierski, M. Z.; Lim, E. C. The Low-Lying ps* State and Its Role in the Intramolecular Charge Transfer of Aminobenzonitriles and Aminobenzethyne. J. Chem. Phys. 2008, 128, 164512 1-11.
- Zgierski, M. Z.; Fujiwara, T.; Lim, E. C. Role of the πσ* State in Molecular Photophysics. Acc. Chem. Res. 2010, 43, 506-517.
- Fujiwara, T.; Zgierski, M. Z.; Lim, E. C. The Role of the ps* State in Intramolecular Charge Transfer of 4-(Dimethylamino)benzonitrile Phys. Chem. Chem. Phys. 2011, 13, 6779-6783.

Experimental studies:

- von der Haar, T.; Hebecker, A.; Il'ichev, Y. V.; Jiang, Y.-B.; Kühnle, W.; Zachariasse, K. A. Excited-state Intramolecular Charge Transfer in Donor/ Acceptor-substituted Aromatic Hydrocarbons and in biaryls. The Significance of the Redox Potentials of the D/A Subsystems. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 430-442.
- Il'ichev, Y. V.; Kühnle, W.; Zachariasse, K. A. Intramolecular charge transfer in dual fluorescent 4-(dialkylamino)benzonitriles. Reaction Efficiency Enhancement by Increasing the Size of the Amino and Benzonitrile Subunits by Alkyl Substituants. *J. Phys. Chem. A* **1998**, *102*, 5670-5680.
- Techert, S.; Zachariasse, K. A. Structure Determination of the Intramolecular Charge Transfer State in Crystalline 4-(Diisopropylamino)benzonitrile from Picosecond X-ray Diffraction. *J. Am. Chem. Soc*. **2004**, *126*, 5593.
- Zachariasse, K. A. 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. *Chem. Phys. Lett.* **2000**, *320*, 8-13.
- Druzhinin S. I.; Jiang, Y.; Demeter, A.; Zachariasse, K. A. Internal conversion with 4-(azetidinyl)benzonitriles in alkane solvents. Influence of fluoro substitution. *Phys. Chem. Chem. Phys.,* **2001**, *3*, 5213-5221.
- Druzhinin S. I.; Kovalenko, S. A.; Senyushkina, T. A.; Zachariasse, K. A. Dynamics of Ultrafast Intramolecular Charge Transfer with 1-*tert*-Butyl-6-cyano-1,2,3,4-tetrahydroquinoline (NTC6) in *n*-Hexane and Acetonitrile. *J. Phys. Chem. A,* **2007**, *111*, 12878-1290.
- Okamoto, H.; Inishi, H.; Nakamura, Y.; Kohtani, S.; Nakagaki, R. Picosecond Infrared Spectra of Isotope-Substituted 4-(Dimethylamino)benzonitriles and Molecular Structure of the Charge-Transfer Singlet Excited State. *J. Phys.Chem. A* **2001**, *105*, 4182-4188.
- Catalan J. On the Dual Emission of p-Dimethylaminobenzonitrile and Its Photophysical Implications. *Phys.Chem. Chem. Phys.* **2013**, *15*, 8811-8820.
- Catalan J. Can the Dipolarity of the Medium Induce the Formation of Charge Transfer Structures? An Unexpected Finding in the Photophysics of DMABN *Phys. Chem. Chem. Phys.* **2014**, *16*, 7734-7740.
- Hicks, J. M.; Vandersall, M. T.; Sitzmann, E. V.; Eisenthal, K. B. Polarity-dependent Barriers and the Photoisomerization Dynamics of Molecules in Solution. *Chem. Phys. Lett.* **1987**, *135*, 413-420.
- Rhinehart, J. M.; Mehlenbacher, R. D.; McCamant, D. Probing the Charge Transfer Reaction Coordinate of 4-(Dimethylamino)benzonitrile with Femtosecond Stimulated Raman Spectroscopy. *J. Phys. Chem. B* **2010,** *114,* 14646–14656
- Rhinehart, J. M.; Challa, J. R.; McCamant, D. W. Multimode Charge-Transfer Dynamics of 4-(Dimethylamino)benzonitrile Probed with Ultraviolet Femtosecond Stimulated Raman Spectroscopy. J. Phys. Chem. B **2012**, *116*, 10522−10534

Solvent dynamics:

- Su, S.-G.; Simon, J. D. The Importance of Vibrational Motion and Solvent Diffusional Motion in Excited State Intramolecular Electron Transfer Reactions. *J. Chem. Phys.* **1988**, *89*, 908.
- Demeter, A.; Druzhinin, S.; George, M.; Haselbach, E., Roulin, J.-L.; Zachariasse, K. A. *Chem. Phys. Lett.* **2000**, *323*, 351.

- Fuss, W.; Pushpa, K. K.; Rettig, W.; Schmid, W. E.; Trushin, S. A. Ultrafast Charge Transfer Via a Conical Intersection in Dimethylaminobenzonitrile. *Photochem. Photobiol. Sci.* **2002**, *1*, 255-262.
- Trushin, S. A.; Yatsuhashi, T.; Fuss, W.; Schmid, W. E. Coherent Oscillations in the Charge-Transfer System 4-dimethylamino-benzonitrile. *Chem. Phys. Lett.* **2003**, *376*, 282-291.
- Yatsuhashi, T.; Trushin, S. A.; Fuss, W.; Rettig, W.; Schmid, W. E.; Zilberg, S. Ultrafast Charge Transfer and Coherent Oscillations in 4-Piperidino-benzonitrile. *Chem. Phys.* **2004**, *296*, 1-12.
- Fuss, W.; Rettig, W.; Schmid, W. E.; Trushin, S. A.; Yatsuhashi, T. Ultrafast Temporary Charge Transfer in Pyrrolidinyl-benzonitrile and Pyrrolyl-benzonitrile in the Gas Phase. *Faraday Discuss.* **2004**, *127*, 23-33.
- Neubauer, A.; Murali, S.; Rettig, W. Charge Transfer Control by Substituents: Donor Pyrroles and Fluoro-anilines. *Int. J. Photoenergy*, **2005**, *7*, 121.
- Changenet, P.; Plaza, P.; Martin, M. M.; Meyer, Y. H. Role of Intramolecular Torsion and Solvent Dynamics in the Charge-transfer Kinetics in Triphenylphosphine Oxide Derivatives and DMABN. *J. Phys. Chem. A* **1997**, *101*, 8186-8194.

Experimental and theoretical studies:

- Murali, S.; Changenet-Barret, P.; Ley, C.; Plaza, P.; Rettig, W.; Martin, M. M.; Tolmachev, A. I. In *Femtochemistry and Femtobiology: Ultrafast Events in Molecular Science*; VIth International Conference on Femtochemistry, Maison de la Chimie, Paris, France, July 6-10, 2003; Martin, M., Hynes, J. T., Eds.; Elsevier: Amsterdam, 2004; p 323.
- Zachariasse, K.A., Druzhinin, S.I., Galievsky, V.A., Kovalenko, S., Senyushkina, T.A., Mayer, P., Noltemeyer, M., Boggio-Pasqua, M., Robb, M. A. Counterintuitive Absence of an Excited-State Intramolecular Charge Transfer Reaction with 2,4,6-Tricyanoanilines. Experimental and Computational Results. *J. Phys. Chem. A* **2009**, *113*, 2693-2710.
- Ma, C.; Kwok, W. M.; Matousek, P.; Parker, A. W.; Phillips, D.; Toner, W. T.; Towrie, M. Excited States of 4-aminobenzonitrile (ABN) and 4-dimethylaminobenzonitrile (DMABN): Time-resolved Resonance Raman, Transient Absorption, Fluorescence, and Ab Initio Calculations. *J. Phys. Chem. A* **2002**, *106*, 3294-3305.

Theoretical studies in solvent:

- Carlotto S., Polimeno A., Ferrante C., Benzi C. Barone, V. Integrated Approach for Modeling the Emission Fluorescence of 4-(N,N-Dimethylamino)benzonitrile-in Polar Environments. *J. Phys. Chem. B* **2008**, *112*, 8106-8113.
- Mennucci, B.; Toniolo, A.; Tomasi, J. Ab Initio Study of the Electronic Excited States in 4-(N,N-dimethylamino)benzonitrile with Inclusion of Solvent Effects: The Internal Charge Transfer Process. *J. Am. Chem. Soc*. **2000**, *122*, 10621-10630.

Theoretical studies:

- Murali, S.; Kharlanov, V.; Rettig, W.; Tolmachev, A. I.; Kropachev, A. V. The Tetrafluoro Analogue of DMABN: Anomalous Fluorescence and Mechanistic Considerations. *J. Phys. Chem. A* **2005**, *109*, 6420-6429.

- Kato, S.; Amatasu, Y. A Theoretical Study on the Mechanism of Charge Transfer State Formation of 4-(N,N-dimethylamino)benzonitrile in an Aqueous Solution. *J. Chem. Phys*. **1990**, *92*, 7241-7257.
- Broo, A.; Zerner, M. C. The Emission Spectum of p-N,N-dimethylaminobenzonitrile. *Chem. Phys. Lett*. **1994**, *227*, 551.
- Scholes, G. D.; Phillips, D.; Gould, I. R. Low-lying Excited States of 4-dimethylaminobenzonitrile: Equilibrium Geometries, Vibrational Frequencies and Charge Transfer Character. *Chem. Phys. Lett*. **1997**, *266*, 521.
- Gedeck, P.; Schneider, S. J. Numerical Self-consistent Reaction Field Study of Intramolecular Charge Transfer in p-(dimethylamino)-benzonitrile. *J. Photochem. Photobiol., A* **1997**, *105*, 165-181.
- Scholes, G. D.; Gould, I. R.; Parker, A. W.; Philips, D. Time-resolved Resonance Raman and Molecular Orbital Studies of Charge Separation and Intramolecular Reorganisation. *Chem. Phys*. **1998**, *234*, 21-34.
- Purkayastha, P.; Bhattacharyya, P. K.; Bera, S. C.; Chattapadhyay, N. Intersystem Crossing (ISC) in DMABN and DMABA: Laser Induced Optoacoustic Spectroscopy and Semi-empirical (AM1) Calculations. *Phys. Chem. Chem. Phys*. **1999**, *1*, 3253-3258.
- Gedeck, P.; Schneider, S. J. Numerical Self-consistent Reaction Field Study of the Excited-state Properties of p-(dimethylamino)-benzonitrile Derivatives. *J. Photochem. Photobiol., A* **1999**, *121*, 7-15.
- Sudholt, W.; Staib, A.; Sobolewski, A. L.; Domcke, W. Molecular-dynamics Simulations of Solvent Effects in the Intramolecular Charge Transfer of 4-(N,N-dimethylamino)benzonitrile. *Phys. Chem. Chem. Phys*. **2000**, *2*, 4341-4353.
- Sudholt, W; Sobolewski, A.; Domcke, W. Ab Initio Study of the Amino Group Twisting and Wagging Reaction Paths in the Intramolecular Charge Transfer of 4-(N,N-dimethylamino)benzonitrile. *Chem. Phys.* **1999**, 240, 9-18.
- Parusel, A. B. J. Density Functional Study of Excited Charge Transfer State Formation in 4-(N,N-dimethylamino)benzonitrile. *J. Phys. Chem. A* **1998**, *102*, 6297-6306.
- Parusel, A. B. J.; Kohler, G.; Nooijen, M. A Coupled-cluster Analysis of the Electronic Excited States in Aminobenzonitriles . *J. Phys. Chem. A* **1999**, *103*, 40564064.
- Parusel, A. B. J. *Phys. Chem. Chem. Phys*. A DFT/MRCI Study on the Excited State Charge Transfer states of N-pyrrolobenzene, N-pyrrolobenzonitrile and 4-N,N-dimethylaminobenzonitrile. **2000**, *24*, 5545-5552.
- Parusel, A. B. J.; Rettig, W.; Sudholt, W. A Comparative Theoretical Study on DMABN: Significance of Excited State Optimized Geometries and Direct Comparison of Methodologies. *J. Phys. Chem. A* **2002**, *106*, 804-815.
- Serrano-Andrés, L.; Merchán, M.; Roos, B. O.; Lindh, R.Theoretical Study of the Internal Charge Transfer in Aminobenzonitriles. *J. Am. Chem. Soc.* **1995**, *117*, 3189-3204.
- Lommatzsch, U.; Brutschy, B. Ab Initio Calculations and Supersonic Jet Studies on the Geometry of 4-dimethylaminobenzonitrile (DMABN) and Related Compounds in the Ground and Excited State. *Chem. Phys.* **1998**, *234*, 35-57.
- Zilberg, S.; Haas, Y. The Nature of the Intramolecular Charge Transfer Excited State in p-pyrrolocyanobenzene (PBN) and Other Derivatives of Benzene Substituted by Electron Donor and Acceptor Groups. *J. Phys. Chem. A* **2002**, *106*, 1-11.
- Cogan S., Zilberg, S.; Haas, Y. The Electronic Origin of the Dual Fluorescence in Donor-acceptor Substituted Benzene Derivatives. *J. Am. Chem. Soc.* **2006**, *128*, 3335-3345.

- Rappoport, D.; Furche, F. Photoinduced Intramolecular Charge Transfer in 4-(Dimethyl)aminobenzonitrile - A Theoretical Perspective. *J. Am. Chem. Soc.* **2004**, *126*, 1277-1284.
- Köhn, A.; Hättig, C. On the Nature of the Low-lying Singlet States of 4-(Dimethyl-amino)benzonitrile. *J. Am. Chem. Soc.* **2004**, *126*, 7399-7410.
- Hättig, C.; Hellweg, A; Köhn, A. Intramolecular Charge-transfer Mechanism in Quinolidines: The Role of the Amino Twist Angle *J. Am. Chem. Soc.* **2006**, *128*, 15672-15682.
- Fonseca, T.; Kim, H. J.; Hynes, J. T. Dynamics of Twisted Intramolecular Charge Transfer Complexes in Polar Solvents. *J. Mol. Liq.* **1994**, *60*, 161-200.
- Fonseca, T.; Kim, H. J.; Hynes, J. T. Twisted Intramolecular Charge Transfer Dynamics in Polar Solvents. *J. Photochem. Photobiol., A: Chem.* **1994**, *82*, 67-79.
- Soujanya, T.; Saroja, G.; Samanta, A. AM1 Study of the Twisted Intramolecular Charge Transfer Phenomenon in p-(N,N-dimethylamino)benzonitrile. *Chem. Phys. Lett.* **1995**, *236*, 503-509.
- Hayashi, S.; Ando, K.; Kato, S. Reaction Dynamics of Charge-transfer State Formation of 4-(N,N-dimethylamino)benzonitrile in a Methanol Solution: Theoretical Analyses. *J. Phys. Chem.* **1995**, *99*, 955-964.
- Kim, H. J.; Hynes, J. T. Excited State Intramolecular Charge Transfer Rates of p-dimethylaminobenzonitrile (DMABN) in Solution: A Two-dimensional Dynamics Perspective. *J. Photochem. Photobiol., A: Chem.* **1997**, *105*, 337-343.
- Gómez, I.; Mercier, Y.; Reguero, M. Theoretical Investigation of Luminescence Behavior as a Function of Alkyl Chain Size in 4-aminobenzonitrile Alicyclic Derivatives. *J. Phys. Chem. A* **2006**, *110*, 11455-11461.
- Jödicke C. J., Lüthi H. P. Time-dependent Density Functional Theory (TDDFT) Study of the Excited Charge-transfer State Formation of a Series of Aromatic Donor-acceptor Systems. *J. Am. Chem. Soc.* **2003**, *125*, 252-264
- McWeeny, R.; Sutcliffe, B. T. *Molecular Quantum Mechanics*; Academic Press: New York, 1969; pp 148-170.

Gaussian package:

- Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

Molcas package

- Aquilante, F.; De Vico, L.; Ferré, N. ; Ghigo, G.; Malmqvist, P. Å.; Neogrády, A.; Bondo Pedersen, T.; Pitoňák, M.; Reiher, M.; Roos, B. O.; Serrano-Andrés, L.; Urban, M.; Veryazov, V. ; Lindh, R. Software News and Update. MOLCAS 7: The Next Generation. *J. Comput. Chem*. **2010**, *31,* 224-247.