

SUPPORTING INFORMATION

Intramolecular Charge Transfer and Dual Fluorescence of 4-(Dimethylamino)benzonitrile: Ultrafast Branching Followed by A Two-fold Decay Mechanism

by

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1. Further computational details.

Several different structures have been analyzed in this work; the ground state DMABN structure (**GS**), the locally excited state (**LE**), and three different charge transfer structures, namely, the $\pi\sigma^*$ state, the twisted intramolecular charge transfer state (**TICT**), and the partially twisted intramolecular charge transfer state (**pTICT**). Moreover, two planar structures (C_{2v} symmetry) C_{2v} (**1**) and C_{2v} (**2**) have also been characterized. C_{2v} (**1**) is a shallow minimum of L_a type that may form after an initial relaxation of the system from the FC region. It has worth mentioning that the use of symmetry during the optimization process, the lack of analytical hessian, and the stabilization energy range (within the accuracy of the method) make this assignment a putative one. C_{2v} (**2**) is the **LE** state optimized in a planar C_{2v} conformation. After inclusion of dynamic correlation this structure is more stable than the pyramidal one both *in vacuo*, a fact already reported in a previous work¹, and in solution. However, the difference in energy lies within the typical error of CASPT2 vertical energy computations, and lacking the possibility of performing a more accurate CASPT2 optimization, we decided to use the pyramidal structure in agreement with previous computational works. It has to be stressed, however, that the geometry of the **LE** state is still an open problem with different existing proposals, planar, pyramidal or twisted^{2,3}, and a careful analysis of the effects that the dynamic correlation and the solvent have in the structure of the **LE** state has still to be performed.

In order to get some insight on the barriers existing in the potential energy surface, linear interpolations in internal coordinates (LIIC) have been performed between the optimized structures of the most significant reaction paths using five intermediate geometries and the same computational protocol as the one used for the equilibrium structures. In the case of the computations including the effect of the solvent, the description provided by the PCM model is expected to be less accurate, due to the limitations of the model and the information is expected to be only qualitative. Furthermore, due to the characteristics of the LIIC the barriers can only be interpreted as an upper limit. The **LE** to **pTICT** LIIC indicates that for this path the barrier (with respect to **LE**) has to be smaller than ~ 1.2 eV with a near degeneracy of the states taking place at about 0.3 eV above the **LE** energy level, which suggests that the barrier can be far smaller than that obtained by the LIIC. The $\pi\sigma^*$ state to **TICT** LIIC displays a more complex structure and does not allow for the characterization of a barrier in

solution due to problems in the identification of the states along the LIIC. However, the *in vacuo* results display a barrier of similar magnitude to the one obtained for the **LE** to **pTICT** LIIC (1.54 eV vs 1.39 eV), yet slightly higher which is in line with the experimentally observed difference in the rise time of the different TICT states. It is expected that solvation will decrease the magnitude of these barriers. Finally, for the **pTICT** to **TICT** LIIC path we found a relatively small barrier of ~0.32 eV (~7.3 kcal/mol). Due to the importance of this barrier, that has to be large enough to allow the fluorescence emission of **pTICT**, we minimized the structure with the highest energy in the LIIC maintaining the relative orientation of the benzonitrile and the dimethylamino group fixed. The structure obtained still displays a barrier of ~0.24 eV (~5.6 kcal/mol). This barrier has to be understood as an upper bound value. Assuming that the real barrier is of this order of magnitude, we can get an estimate for the lifetime of this intermediate (at 298.15 K and assuming a frequency factor of 10^{12} – 10^{13} s⁻¹) as $\tau \approx (10^{13} e^{-5.0/RT})^{-1} \approx 1.2$ ns, that is in the order of magnitude of the fluorescence emission lifetime. Moreover, it has to be taken into account that a) the rough estimate of the lifetime assumes equilibrium solvation of the solvent, so it is expected that a real treatment involving non-equilibrium solvation will render a larger lifetime and b) the reaction coordinate for the transformation **pTICT** to **TICT** implies a conformational change where a moderately large amplitude oscillation of the dimethylamino group (which is polar and it is expected to have sensible microscopic interactions with solvent molecules in the first solvation shell) is taking place. The solvent dynamics can therefore affect the barrier for this kind of process. These effects, however, cannot be taken into account appropriately with this model and its evaluation would need the computation of a statistical meaningful set of molecular dynamics trajectories with explicit solvent consideration and non-equilibrium conditions, something that it is nowadays a formidable computational challenge.

Table S1 contains the *in vacuo* and in solution (acetonitrile) vertical Franck-Condon (FC) energies (in eV) of the ¹L_a and ¹L_b states. As can be seen, the *in vacuo* results render the (bright) ¹L_a state energetically less stable than ¹L_b while in solution both states approach due to the differential stabilization of the polar solute in the polar solvent (acetonitrile). This stabilization makes possible the dual fluorescence phenomenon by decreasing the barriers (or conical intersection seams) for the conversion process between the **LE** and the fluorescent charge transfer state (**pTICT**) in

a polar solvent. *In vacuo*, such stabilization is not present and then the phenomenon is not observed. Table S2 compiles the results for the two C_{2v} structures discussed in the text, both in solution and *in vacuo*. Table S3 contains the absolute CASPT2 energies for all optimized structures. Finally, Table S4 compiles their Cartesian coordinates.

2. Further experimental details.

Temporal decay profiles at specific wavelengths were analyzed by deconvolution procedures with nonlinear least-squares fitting. The multiple-exponential model function $\sum_i^n A_i \exp(-t/\tau_i) + A_\infty$ was analytically convoluted with a Gaussian function (for TA decay analysis) or with a Voigt function (for TR-FS decay analysis), whose temporal width was also one of fit parameters to be optimized, to model the instrument response function. A long-live component (nanoseconds) due to the triplet–triplet absorption was treated as the background of A_∞ in the fitting function for a short time window (tens picosecond) data. Prior to kinetic analysis, relevant TA data was prepared by band-integration from the fully mapped 2D spectra. In all the experimental setups, relative polarizations of the pump–probe beams in TA as well as those of the pump to the 1st intake polarizer in OKG were set at magic angle (54.7°). Correction for the temporal dispersion of the mapped TA and OKG data was made by numerically applying a correction curve that was created in a prior observation of GVD for each setup. Spectral response to the wavelengths was not corrected.

References:

1. J. Dreyer, A. Kummrow, 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.
2. I. Gómez, M. Reguero, M. Boggio-Pasqua, M. A. Robb, (2005) Intramolecular Charge Transfer in 4-Aminobenzonitriles does not necessarily Need the Twist, *J. Am. Chem. Soc.* 2005, **127**, 7119-7129.
3. A. Köhn, C. Hättig, (2004) On the Nature of the Low-Lying Singlet States of 4-(Dimethylamino)benzonitrile, *J. Am. Chem. Soc.* 2004, **126**, 7399-7410.

Table S1. Vertical energies (ΔE , eV) and oscillator strengths (f) of 1L_a and 1L_b states evaluated at the FC geometry *in vacuo* and in solution.

System	<i>In Vacuo</i>		Solution	
	ΔE	f	ΔE	f
1L_a	4.41	0.435	4.16	0.401
1L_b	4.09	0.007	4.05	0.007

Table S2. *In vacuo* and in solution (acetonitrile) adiabatic energies (ΔE , eV), relative to GS and modulus of the dipole moment (in Debye) for the different C_{2v} structures analyzed.

System	<i>In Vacuo</i>		Solution	
	ΔE	$ \mu $	ΔE	$ \mu $
$C_{2v}(1)$	4.14	13.599	3.79	17.385
$C_{2v}(2)$	3.81	6.763	3.70	8.460

Table S3. Transition dipole moment components (TDM_{*i*}, au) and *in vacuo* and in solution oscillator strengths for the different ICT analyzed.

System	<i>In Vacuo</i>			<i>In Vacuo</i>	Solution
	TDM _x	TDM _y	TDM _z	f	f
TICT	-0.005	0.127	-0.013	0.001	0.001
pTICT	1.758	0.000	0.000	0.260	0.231

Table S4. Absolute *in vacuo* and in solution (acetonitrile) CASPT2 energies (au) for all the structures analyzed.

System	E_{vac}	E_{sol}
GS	-457.2005898	-457.0564007
LE	-457.0580421	-457.0734698
$\pi\sigma^*$	-457.0195907	-457.0717348
TICT	-457.0610363	-457.0934534
pTICT	-457.0564007	-457.0817805
$C_{2v}(1)$	-457.0482849	-457.0747663
$C_{2v}(2)$	-457.0603283	-457.0779889

Table S5. Cartesian coordinates (bohr) for the different systems analyzed in this work.

GS			
Atom	X	Y	Z
C	-2.2286788906	0.0002911543	-0.5251516819
C	-0.8278860499	-2.2731143009	-0.4756339670
C	-0.8284889958	2.2740705476	-0.4757460884
C	1.8003899604	-2.2695935567	-0.3417960651
C	1.7997910983	2.2712675897	-0.3419117099
C	3.1444345814	0.0010096948	-0.2679280146
C	-6.0999544352	-2.3018789786	-1.3410468241
C	-6.1006237949	2.3014396891	-1.3407282405
C	5.8955152531	0.0013219574	-0.1352169786
N	-4.8410702963	-0.0000886935	-0.5413852278
N	8.0792470148	0.0015337218	-0.0286694045
H	-8.1199124809	-2.0043315302	-1.2682273770
H	-8.1204983052	2.0033637602	-1.2677392009
H	-5.6025259355	-2.8794581677	-3.2591367614
H	-5.6035189210	2.8793228793	-3.2588126911
H	-5.6861114167	-3.8479011277	-0.0662989427
H	-5.6870468687	3.8474504717	-0.0658821092
H	2.7963854558	-4.0359156105	-0.3033543806
H	2.7953393923	4.0378521501	-0.3035797259
H	-1.7668761519	-4.0608850458	-0.5336374036
H	-1.7679735510	4.0615793125	-0.5338655555

LE			
Atom	X	Y	Z
C	-2.2148248442	0.0002733625	-0.6238533857
C	-0.8384512436	-2.3356288206	-0.5262060785
C	-0.8390689565	2.3365511094	-0.5264230809
C	1.8654833348	-2.3414553468	-0.3401774822
C	1.8648680117	2.3431278906	-0.3404231782
C	3.2016459635	0.0010149974	-0.2444280530
C	-6.1432164776	-2.3097930139	-1.3404819548
C	-6.1438834093	2.3093590888	-1.3400152076
C	5.9262839226	0.0013463938	-0.0533890711
N	-4.8169932665	-0.0000879542	-0.6863538353
N	8.1120924859	0.0015560790	0.0993104243
H	-8.1514868402	-1.9920607597	-1.1447597182
H	-8.1520507455	1.9910716160	-1.1441328975
H	-5.7681481397	-2.9178481001	-3.2738290069
H	-5.7691768595	2.9178044658	-3.2733115322
H	-5.6474773731	-3.8275221613	-0.0650266012
H	-5.6484042881	3.8270203758	-0.0643781648
H	2.8837959623	-4.0888853462	-0.2773193752
H	2.8827258543	4.0908342905	-0.2778310570
H	-1.7863413749	-4.1130417908	-0.6161363201
H	-1.7874350540	4.1136995411	-0.6165827737

Table S5 (cont.)

$\pi\sigma^*$			
Atom	X	Y	Z
C	-2.0883296807	-0.0844246797	0.0000000000
C	-0.7641000454	-2.4434344873	0.0000000000
C	-0.6188074450	2.1838354502	0.0000000000
C	1.8163432589	-2.5060658520	0.0000000000
C	1.9648358561	2.0794017886	0.0000000000
C	3.2869467026	-0.2511852828	0.0000000000
C	-6.1097807926	-2.3245370955	0.0000000000
C	-5.9586961123	2.4075213665	0.0000000000
C	6.1124918228	-0.2896190360	0.0000000000
N	-4.6182061507	-0.0034997201	0.0000000000
N	7.3044400216	-2.3122566988	0.0000000000
H	-8.0884233695	-1.8392635463	0.0000000000
H	-7.9642876565	2.0499936591	0.0000000000
H	-5.7191295826	-3.4443825174	1.6699246991
H	-5.4971835444	3.5006259120	1.6697320542
H	2.8090785837	-4.2722039762	0.0000000000
H	3.0576344379	3.7876279851	0.0000000000
H	-1.7948564090	-4.1834388653	0.0000000000
H	-1.5352776829	3.9862013867	0.0000000000
H	-5.7191295826	-3.4443825174	-1.6699246991
H	-5.4971835444	3.5006259120	-1.6697320542

TICT			
Atom	X	Y	Z
C	-2.1721466438	0.1387795389	0.6402880125
C	-0.8396651939	-2.2289784215	0.3980717130
C	-0.8161621107	2.4035435950	-0.0473718922
C	1.7086073985	-2.2749016064	-0.1143168665
C	1.7317745148	2.3250022704	-0.5563697053
C	3.0751578234	-0.0064929751	-0.5925347492
C	-5.4260851918	-0.1821181679	-2.7939041992
C	-6.6939079401	0.2616475217	1.7698175864
C	5.7446407538	-0.0710477573	-1.1248604291
N	-4.7507772661	0.0750733224	-0.1376934751
N	7.8937123168	-0.1243414182	-1.5656503692
H	-7.4528292552	-0.1303830497	-3.0340238340
H	-8.5604395406	0.1582532632	0.9482660681
H	-4.5450893327	1.3410061556	-3.8381282402
H	-6.4394464508	2.0363207370	2.7669431790
H	-4.6752918294	-1.9566115167	-3.4861916186
H	-6.4101941261	-1.2550155513	3.1204762057
H	2.6992734513	-4.0461910793	-0.0923348723
H	2.7401309982	4.0578201838	-0.8725273300
H	-1.8197993595	-3.9757415388	0.7425055295
H	-1.7783040163	4.1936514940	-0.0437677135

Table S5 (cont.)

pTICT			
Atom	X	Y	Z
C	-2.0966428038	0.0000000000	0.0000000000
C	-0.7379835300	-2.3427351379	0.0031933645
C	-0.7379835300	2.3427351379	-0.0031933645
C	1.8608153487	-2.3319711282	0.0213660378
C	1.8608153487	2.3319711282	-0.0213660378
C	3.2417554271	0.0000000000	0.0000000000
C	-6.1261714367	-1.3650029987	-1.9010621821
C	-6.1261714367	1.3650029987	1.9010621821
C	5.9533602348	0.0000000000	0.0000000000
N	-4.7175467197	0.0000000000	0.0000000000
N	8.1528682615	0.0000000000	0.0000000000
H	-7.9220158899	-1.9830791142	-1.1425574714
H	-7.9220158899	1.9830791142	1.1425574714
H	-6.4554873028	-0.1009939627	-3.4948756640
H	-5.0317477459	2.9564801395	2.5572042391
H	-5.0317477459	-2.9564801395	-2.5572042391
H	-6.4554873028	0.1009939627	3.4948756640
H	2.8649701153	-4.0933185636	0.0417439495
H	2.8649701153	4.0933185636	-0.0417439495
H	-1.7440901962	-4.1024147192	0.1037119145
H	-1.7440901962	4.1024147192	-0.1037119145

C_{2v}(1)			
Atom	X	Y	Z
C	-2.1293615335	0.0000000000	0.0000000000
C	-0.7356662754	-2.3550748653	0.0000000000
C	1.8563444507	-2.3467478855	0.0000000000
C	3.2545389830	0.0000000000	0.0000000000
C	-6.1064199162	-2.3560648281	0.0000000000
C	5.9334024707	0.0000000000	0.0000000000
C	-0.7356662754	2.3550748653	0.0000000000
C	1.8563444507	2.3467478855	0.0000000000
C	-6.1064199162	2.3560648281	0.0000000000
N	-4.6906025770	0.0000000000	0.0000000000
N	8.1494746657	0.0000000000	0.0000000000
H	-8.0991708113	-1.9363832830	0.0000000000
H	-5.6672795970	-3.4629076293	1.6683012373
H	2.8564998259	-4.1089892329	0.0000000000
H	-1.7205675217	-4.1203445132	0.0000000000
H	-8.0991708113	1.9363832830	0.0000000000
H	-5.6672795970	3.4629076293	-1.6683012373
H	-5.6672795970	-3.4629076293	-1.6683012373
H	-5.6672795970	3.4629076293	1.6683012373
H	2.8564998259	4.1089892329	0.0000000000
H	-1.7205675217	4.1203445132	0.0000000000

Table S5 (cont.)

Atom	$C_{2v}(2)$		
	X	Y	Z
C	-2.1320188222	0.0000000000	0.0000000000
C	-0.7811168024	-2.3401924104	0.0000000000
C	1.9219604269	-2.3432014339	0.0000000000
C	3.2447703214	0.0000000000	0.0000000000
C	-6.1201582535	-2.3536449063	0.0000000000
C	5.9806282695	0.0000000000	0.0000000000
C	-0.7811168024	2.3401924104	0.0000000000
C	1.9219604269	2.3432014339	0.0000000000
C	-6.1201582535	2.3536449063	0.0000000000
N	-4.7178360704	0.0000000000	0.0000000000
N	8.1726389503	0.0000000000	0.0000000000
H	-8.1179631406	-1.9422392886	0.0000000000
H	-5.7023490326	-3.4751033234	1.6672027774
H	2.9517879601	-4.0850716101	0.0000000000
H	-1.7487168870	-4.1106110380	0.0000000000
H	-8.1179631406	1.9422392886	0.0000000000
H	-5.7023490326	3.4751033234	-1.6672027774
H	-5.7023490326	-3.4751033234	-1.6672027774
H	-5.7023490326	3.4751033234	1.6672027774
H	2.9517879601	4.0850716101	0.0000000000
H	-1.7487168870	4.1106110380	0.0000000000

Table S6. Mulliken charges *in vacuo* and in solution (acetonitrile) for the most significant structures discussed in the manuscript.

GS		
Atom	Mulliken charges in vacuo	Mulliken charges in solution
C	-0.0504	-0.0700
C	-0.1976	-0.2153
C	-0.1976	-0.2152
C	-0.0788	-0.0917
C	-0.0788	-0.0918
C	0.0783	0.0510
C	-0.1209	-0.1463
C	-0.1209	-0.1461
C	0.1044	0.1616
N	0.1725	0.1570
N	-0.1916	-0.2757
H	0.1025	0.1231
H	0.1025	0.1230
H	-0.0055	0.0067
H	-0.0056	0.0065
H	0.0442	0.0585
H	0.0443	0.0585
H	0.1032	0.1270
H	0.1032	0.1271
H	0.0962	0.1261
H	0.0962	0.1260

LE		
Atom	Mulliken charges in vacuo	Mulliken charges in solution
C	-0.1371	-0.1683
C	-0.2203	-0.2476
C	-0.2203	-0.2476
C	-0.1143	-0.1322
C	-0.1143	-0.1322
C	0.1170	0.1075
C	-0.1142	-0.1389
C	-0.1142	-0.1386
C	0.1166	0.1709
N	0.2878	0.2924
N	-0.1786	-0.2576
H	0.1003	0.1247
H	0.1003	0.1247
H	-0.0087	0.0032
H	-0.0087	0.0030
H	0.0473	0.0608
H	0.0473	0.0608
H	0.1072	0.1290
H	0.1072	0.1290
H	0.0998	0.1284
H	0.0998	0.1284

Table S6 (cont.)

$\pi\sigma^*$		
Atom	Mulliken charges in vacuo	Mulliken charges in solution
C	-0.0836	-0.0929
C	-0.2142	-0.1848
C	-0.2062	-0.1733
C	-0.0533	-0.0829
C	-0.0337	-0.0695
C	0.2095	0.2109
C	-0.1020	-0.1334
C	-0.1019	-0.1340
C	-0.2267	-0.3494
N	0.4156	0.5536
N	-0.2643	-0.4503
H	0.1179	0.1532
H	0.1184	0.1534
H	0.0118	0.0365
H	0.0113	0.0367
H	0.1187	0.1106
H	0.0950	0.1009
H	0.0821	0.1205
H	0.0825	0.1215
H	0.0118	0.0361
H	0.0113	0.0365

TICT		
Atom	Mulliken charges in vacuo	Mulliken charges in solution
C	-0.3100	-0.3056
C	-0.2681	-0.2724
C	-0.2674	-0.2710
C	-0.1118	-0.1453
C	-0.1114	-0.1452
C	-0.0318	-0.0680
C	-0.0971	-0.1199
C	-0.0654	-0.0912
C	0.1015	0.1460
N	0.6192	0.6739
N	-0.2352	-0.3282
H	0.0672	0.0832
H	0.0851	0.1006
H	0.0595	0.0683
H	0.0404	0.0498
H	0.0548	0.0632
H	0.0433	0.0534
H	0.1044	0.1277
H	0.1044	0.1280
H	0.1090	0.1263
H	0.1094	0.1265

Table S6 (cont.)

pTICT

Atom	Mulliken charges in vacuo	Mulliken charges in solution
C	-0.2103	-0.2074
C	-0.2284	-0.2350
C	-0.2281	-0.2351
C	-0.1152	-0.1357
C	-0.1153	-0.1357
C	-0.0472	-0.0773
C	-0.1018	-0.1226
C	-0.1016	-0.1228
C	0.0912	0.1380
N	0.5834	0.5879
N	-0.2525	-0.3439
H	0.0517	0.0653
H	0.0517	0.0651
H	0.0171	0.0210
H	0.0947	0.1102
H	0.0947	0.1103
H	0.0171	0.0214
H	0.1000	0.1236
H	0.1000	0.1236
H	0.0995	0.1244
H	0.0994	0.1245