Electronic Supplementary Information

(Total of 6 pages)

for

A Theoretical Study of the Intramolecular Charge Transfer in 4-(Dimethylamino)benzethyne

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Table S1. CASSCF/ANO-S-VDZP optimized Franck-Condon ground-state geometry (in Å) of the DMABE *in vacuo*.

C1	-0.50031472	-0.81399696	0.08253325
C2	0.90743828	-0.81399696	0.08253325
C3	-1.13601209	0.44205024	0.08253325
C4	1.63321653	0.37069988	0.09943359
C5	-0.40671380	1.62459127	0.09904284
C6	0.99075602	1.61180515	0.11055542
C7	-0.55000589	-3.21135226	-0.31294915
C8	-2.61701642	-1.94084057	-0.31243548
C9	1.75442670	2.85421910	0.12430259
C10	2.38845605	3.88579059	0.13752807
N11	-1.23501325	-2.00929192	0.12085693
H12	-1.23539427	-4.04565969	-0.24970367
H13	-3.05187628	-2.92913806	-0.24926044
H14	-0.18129385	-3.14682596	-1.33968101
H15	-2.72632932	-1.58248688	-1.33904235
H16	0.28440196	-3.43904939	0.33810297
H17	-3.19674305	-1.29932349	0.33896621
H18	2.70600049	0.32820727	0.10075068
H19	-0.92905708	2.56258374	0.09968714
H20	1.45331028	-1.73393148	0.07315797
H21	-2.20331039	0.51368567	0.07335548
H22	2.94000044	4.78316484	0.14920283

Table S2. CASSCF/ANO-S-VDZP optimized Locally Excited (LE) excited-state minimum geometry (in Å) of the DMABE *in vacuo*.

C1	-0.49200815	-0.82770775	0.06536454
C2	0.94241185	-0.82770775	0.06536454
C3	-1.17737549	0.43238330	0.06536454
C4	1.67606159	0.40239202	0.06073789
C5	-0.44731597	1.66461608	0.06073576
C6	0.98529522	1.65748795	0.05936354
C7	-0.51883321	-3.25207545	-0.20624175
C8	-2.60899261	-2.00958764	-0.20589889
C9	1.71941886	2.89247887	0.05540936
C10	2.34033863	3.93705032	0.05085739
N11	-1.20199009	-2.02208397	0.14589045
H12	-1.19261061	-4.08265686	-0.04579745
H13	-3.01667497	-2.99834217	-0.04545808
H14	-0.19256591	-3.27085345	-1.24803723
H15	-2.78163496	-1.73183858	-1.24762384
H16	0.34140106	-3.41383817	0.42897320
H17	-3.16194607	-1.33124469	0.42952513
H18	2.74714732	0.38662719	0.05561281
H19	-0.97293267	2.59799698	0.05557670
H20	1.49483718	-1.74104785	0.06049467

H21	-2.24366488	0.48127435	0.06044524
H22	2.87857080	4.84253135	0.04871416

Table S3. CASSCF/ANO-S-VDZP optimized πσ* excited-state minimum geometry (in Å) of the DMABE *in vacuo*.

C1	-1.10898	-0.04492	0.00000
C2	-0.41184	-1.28824	0.00000
C3	-0.32826	1.14438	0.00000
C4	0.95667	-1.33568	0.00000
C5	1.04201	1.09109	0.00000
C6	1.74961	-0.14623	0.00000
C7	-3.24544	-1.22247	0.00000
C8	-3.15867	1.27637	0.00000
C9	3.17999	-0.16030	0.00000
C10	3.96286	-1.25735	0.00000
N11	-2.46340	0.00155	0.00000
H12	-4.29453	-0.97009	0.00000
H13	-4.22278	1.09776	0.00000
H14	-3.04376	-1.82214	0.88257
H15	-3.04376	-1.82214	-0.88257
H16	-2.91589	1.86075	0.88267
H17	-2.91589	1.86075	-0.88267
H18	1.46976	-2.27605	0.00000
H19	1.61286	1.99954	0.00000
H20	-0.95764	-2.20900	0.00000
H21	-0.80648	2.10185	0.00000
H22	5.04232	-1.17072	0.00000

Table S4. CASSCF/ANO-S-VDZP optimized partially-Twisted Intramolecular Charge Transfer (pTICT) excited-state minimum geometry (in Å) of the DMABE *in vacuo*.

C1	-0.47195548	-0.80403208	0.00000030
C2	0.96453852	-0.80403208	0.00000030
C3	-1.17222020	0.45021843	0.00000030
C4	1.64942546	0.38292064	0.01347886
C5	-0.46972239	1.62683379	-0.01347826
C6	0.96502553	1.64402972	0.00000030
C7	-0.93553384	-2.99326291	-1.01296678
C8	-2.15746320	-2.27600454	1.01296502
C9	1.68881397	2.87708911	0.00000030
C10	2.30724987	3.93066607	0.00000030
N11	-1.16912878	-1.99174628	0.00000030
H12	-1.13564619	-3.98155778	-0.61899989
H13	-2.92282420	-2.93250567	0.61899746
H14	-1.60388221	-2.79959378	-1.85372462
H15	-2.59201041	-1.35372079	1.36823137

H16	0.08157513	-2.92308402	-1.36823716
H17	-1.66255966	-2.76514941	1.85372523
H18	2.72289567	0.36884267	0.02915744
H19	-1.00531155	2.55725345	-0.02915683
H20	1.49810668	-1.73509468	0.04974844
H21	-2.24526659	0.46221837	-0.04974783
H22	2.83987538	4.83805862	0.00000030

Table S5. CASSCF/ANO-S-VDZP optimized Twisted Intramolecular Charge Transfer (TICT) excited-state minimum geometry (in Å) of the DMABE *in vacuo*.

C1	-1.12005	0.00000	0.00000
C2	-0.40337	-1.24102	0.00000
C3	-0.40337	1.24102	0.00000
C4	0.96351	-1.22876	0.00000
C5	0.96351	1.22876	0.00000
C6	1.70546	0.00000	0.00000
C7	-3.25082	0.00000	-1.25849
C8	-3.25082	0.00000	1.25849
C9	3.13905	0.00000	0.00000
C10	4.36293	0.00000	0.00000
N11	-2.52853	0.00000	0.00000
H12	-4.32092	0.00000	-1.10437
H13	-4.32092	0.00000	1.10437
H14	-2.93870	0.87656	-1.81530
H15	-2.93870	-0.87656	1.81530
H16	-2.93870	0.87656	1.81530
H17	-2.93870	-0.87656	-1.81530
H18	1.49705	-2.16120	0.00000
H19	1.49705	2.16120	0.00000
H20	-0.93303	-2.17777	0.00000
H21	-0.93303	2.17777	0.00000
H22	5.41446	0.00000	0.00000

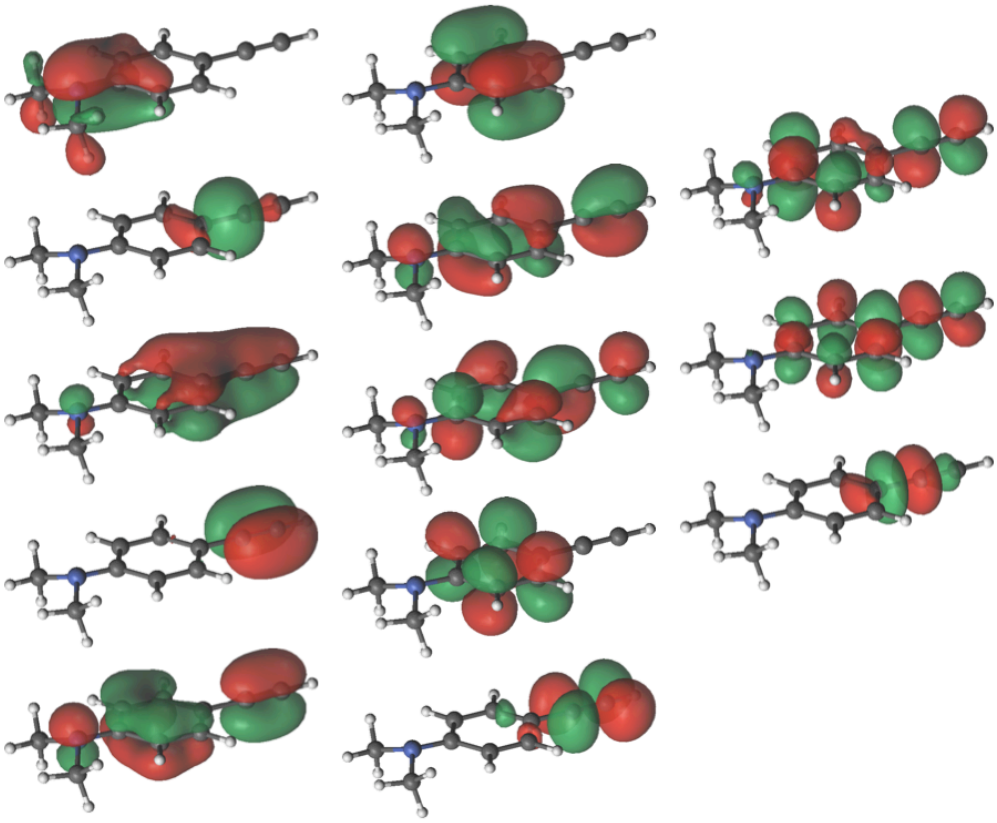

Figure S1. Orbitals comprising the (14,13) active space employed in the CASSCF calculations of DMABE.