CASPT2, CASSCF and Non-Adiabatic Molecular Dynamics (NAMD) studies on the low-lying electronic states of 1*H*-1,2,3-Triazoles Photolysis

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SUPPLEMENTARY INFORMATION

XYZ coordinates of 1*H*-1,2,3-Benzotriazole : SA4-CASSCF(14,12)/ANO-S-VDZP level.

C -0.00188097 0.00293590 0.00000136
C -0.83948169 1.10887365 -0.00002575
C -2.22399431 0.84670138 -0.00007469
C -2.73463148 -0.45257035 -0.00002346
C -1.87645643 -1.57082296 -0.00001290
C -0.51235251 -1.32537130 0.00000942
H 0.18290242 -2.15247691 0.00002645
H -2.27488168 -2.57477732 -0.00002347
N -4.10384962 -0.38838953 -0.00000168
N -4.46167696 0.83334118 0.00008253
N -3.32484136 1.63060407 0.00001422
H -3.42569577 2.62381420 -0.00001050
H -0.44480033 2.11420712 -0.00000159
H 1.06864463 0.15254488 0.00004007

XYZ coordinates of conical intersection of the 1*H*-1,2,3-Benzotriazole : MS3-CASPT2(12,11)/ANO-L-VDZP level.

C 0.00483156 0.02839657 -0.03127060
C -0.85503612 1.12658912 -0.01560026
C -2.28950501 0.97156508 -0.01189440
C -2.78152257 -0.39007704 0.02147132
C -1.91530840 -1.48392596 0.01425216
C -0.51700533 -1.28609262 0.01563717
H 0.15484491 -2.14593869 0.05338498
H -2.34205661 -2.48957025 0.01515049
N -4.17280033 -0.71005365 -0.02483973
N -5.11135324 0.03588411 -0.09879474
N -3.15722742 1.98887460 0.09261501
H -2.62380718 2.87351077 0.05036465
H -0.45256328 2.14366806 -0.00032041
H 1.08551314 0.18578385 -0.08015559

XYZ coordinates of the open-ring benzotriazole : SA4-CASSCF(14,13)/ANO-S-VDZP level.

C	-0.01655058	0.04168518	-0.00322528
C	-0.80063858	1.14992006	-0.00722830
C	-2.26905360	1.06738655	-0.00404119
C	-2.78448083	-0.30388306	0.00363944
C	-1.92987621	-1.47076463	0.00800019
C	-0.58211396	-1.30305916	0.00425656
H	0.07716922	-2.15785253	0.00702686
H	-2.38058621	-2.45265235	0.01329325
N	-4.10955135	-0.46275203	0.00653833
N	-5.24202623	-0.55939362	0.00910625
N	-3.07421204	2.07131443	-0.00746989
H	-2.55917060	2.93978944	-0.01283184
H	-0.36115158	2.13775118	-0.01205073
H	1.05924658	0.15112461	-0.00501373

Open-ring benzotriazole: SA4-CASSCF(14,13)/ANO-S-VDZP level with the C1-N3 bond constrained at 1.65 Å.

C	0.01048008	0.04534730	0.02922514
C	-0.77735122	1.15231930	-0.05299705
C	-2.24399645	1.05582759	-0.11825515
C	-2.70887732	-0.30997410	-0.33089212
C	-1.90824279	-1.45985820	-0.04304029
C	-0.55434035	-1.29378429	0.04803103
H	0.10174678	-2.15002091	0.09553549
H	-2.35664633	-2.44306060	-0.05238719
N	-4.27296861	-0.47154354	0.16912162
N	-5.38734643	-0.54592322	0.10595582
N	-3.06123671	2.05077613	-0.02791348
H	-2.55069748	2.91631762	0.07126697
H	-0.34645402	2.14294344	-0.00166300
H	1.08293488	0.15924754	0.10801217

XYZ coordinates of open-ring benzotriazole: SA4-CASSCF(14,13)/ANO-S-VDZP level with the C1-N3 bond constrained at 1.85 Å.

C	0.03267983	0.04735755	0.06313269
C	-0.77231250	1.15294458	-0.01846877
C	-2.21682241	1.02332016	-0.18510508
C	-2.69813894	-0.33531634	-0.36771509
C	-1.90579588	-1.44598432	-0.06045175
C	-0.52617771	-1.27241480	0.02878362
H	0.13008162	-2.13075367	0.01450859
H	-2.33308351	-2.44001224	-0.07093839
N	-4.37403204	-0.48574387	0.40121525
N	-5.45306060	-0.50309704	0.13633292
N	-3.04872801	2.02996823	-0.18332791
H	-2.54329508	2.89727907	-0.06207603
H	-0.36418872	2.14605279	0.11384790

H	1.09987798	0.16501397	0.19026198

XYZ coordinates of open-ring benzotriazole: SA4-CASSCF(14,13)/ANO-S-VDZP level with the C1-N3 bond constrained at 2.15 Å.

C	0.07385635	0.03024973	0.06659924
C	-0.76813258	1.15345832	-0.00098498
C	-2.18171283	1.00727588	-0.16382204
C	-2.66412232	-0.34337809	-0.24721733
C	-1.87452391	-1.44186535	-0.10504234
C	-0.45555275	-1.25805867	0.01208392
H	0.19835036	-2.11802675	0.03058362
H	-2.29319621	-2.43940175	-0.12239687
N	-4.63283331	-0.57883933	0.58418813
N	-5.58039327	-0.40688417	0.03988552
N	-3.04125238	2.02514452	-0.22214242
H	-2.53789827	2.89948154	-0.13965018
H	-0.35623258	2.14865292	0.09857907
H	1.14064767	0.17080527	0.16933664

XYZ coordinates of open-ring benzotriazole: SA4-CASSCF(14,13)/ANO-S-VDZP level with the C1-N3 bond constrained at 2.35 Å.

C	0.10575514	0.03098096	-0.00084857
C	-0.71147477	1.17852857	-0.04301546
C	-2.13260969	1.07184564	-0.05774281
C	-2.64537342	-0.26795588	-0.02467636
C	-1.88507222	-1.38962302	0.01906119
C	-0.45134961	-1.23934382	0.02986458
H	0.18040257	-2.11517676	0.06138852
H	-2.33455637	-2.37215772	0.04493788
N	-4.85664999	-1.05283556	0.10462880
N	-5.73961245	-0.38989088	0.13217258
N	-2.97459865	2.11017911	-0.09665797
H	-2.44553926	2.97315314	-0.11440123
H	-0.26268629	2.16259354	-0.06259815
H	1.18036898	0.14831678	0.00788700

XYZ coordinates of *2H*-1,2,3-Benzotriazole : SA4-CASSCF(12,10)/ANO-S-VDZP level.

<u>S0 geometry:</u>

C	-0.00734054	0.01405985	0.00000081
C	1.43765824	0.09709170	0.00000099
C	2.09720821	1.30056005	-0.00000074
C	1.28530286	2.47610577	0.00000108
C	-0.12921613	2.39537983	0.00000055
C	-0.80187022	1.13125102	-0.00000073
H	-1.87992174	1.07120737	-0.00000257
N	-0.61728727	3.63481206	-0.00000177
N	0.46709428	4.37789351	0.00000211

N	1.62850885	3.76512310	-0.00000199
H	0.40871770	5.37701387	0.00000244
H	3.17504204	1.36586349	-0.00000257
H	2.00326438	-0.82402050	0.00000149
H	-0.46312099	-0.96620959	0.00000148

S1 geometry:

C	-0.00527665	-0.02799967	-0.00000022
C	1.44072041	0.05546678	0.00000033
C	2.11970843	1.32828963	-0.00000021
C	1.31935964	2.46395441	-0.00000146
C	-0.16178020	2.37847026	0.00000232
C	-0.82616284	1.15829497	0.00000038
H	-1.90315966	1.09471341	-0.00000054
N	-0.64266037	3.65523581	0.00000060
N	0.46484840	4.39565977	0.00000123
N	1.65017278	3.78756159	-0.00000139
H	0.40724835	5.39358068	-0.00000069
H	3.19686581	1.38905432	0.00000069
H	2.01707900	-0.85621661	0.00000081
H	-0.47292344	-0.99993382	-0.00000130

XYZ coordinates of the open-ring Triazole : G4 level.

C 0.00000000 0.00000000 0.00000000
C -1.34140000 0.54394200 0.00070100
N -2.36626600 -0.26527300 0.00103700
N -3.22515200 -1.00152500 0.00001100
H -1.57091900 1.59852800 0.00028300
N 0.24449700 -1.25470300 0.00067300
H 1.24961900 -1.42232200 0.00078900
H 0.76700100 0.78545600 -0.00014700

XYZ coordinates of the TS: G4 level.

C 0.00000000 0.00000000 0.00000000
C 0.98123000 0.96341700 -0.14657200
H 1.10875900 1.60347100 0.73616000
N -0.20354100 -1.24966800 0.08287400
H -1.18958900 -1.48554100 -0.00619200
H -0.80168300 0.80348800 -0.16818300
N 2.79515800 -0.17386700 0.22464100
N 3.70140400 -0.69620400 -0.11436700

XYZ coordinates of the ethanamine: G4 level.

C 0.00000000 0.00000000 0.00000000
C 0.00007900 1.31869800 0.00000000
N 0.00015700 2.50425800 0.00000000
H 0.00023000 3.49126200 0.00000000
H 0.93477800 -0.54182000 0.00000000

H -0.93484400 -0.54170600 0.00000000

XYZ coordinates of the N_2: G4 level.
N 0.00000000 0.00000000 0.00000000
N 0.00000000 0.00000000 -1.09879200

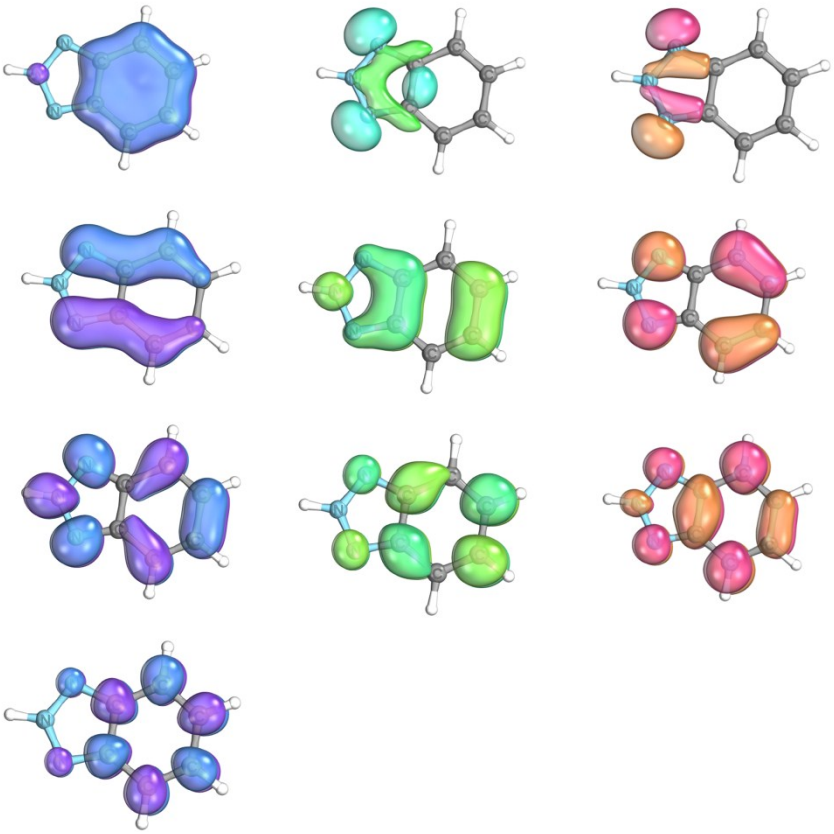

Figure S1. Active space for the 2*H*-1,2,3-benzotriazole calculated at the SA(4)-CASSCF(12,10)/ANO-S-VDZP level of theory.

Tabela S1. Excitation energies (Ev_{ert} (eV)) and oscillator strengths (f_{osc}) of the first six singlet excited states of 1*H*-1,2,3-bentriazole obtained with RI-CC2 and EOM-CCSD with the aug-cc-pVDZ basis set.

	RI-CC2		**EOM-CCSD**	
	Ev_{ert}	f_{osc}	Ev_{ert}	f_{osc}
S_1	4.86	0.0784	4.86	0.0703
S_2	5.38	0.0053	5.56	0.0073
S_3	5.55	0.0817	5.74	0.0849
S_4	5.85	0.0000	5.99	0.0002
S_5	6.29	0.0004	6.43	0.0037

S_6	6.31	0.0084	6.46	0.0062