Supplementary Data

A study of 1-methylbenzotriazole (MEBTA) using quantum mechanical calculations and vibrational, electronic, and nuclear magnetic resonance spectroscopies

Table S1. B3LYP/6-31G(d,p) optimized geometry of MEBTA. The X, Y, and Z coordinates are in Å.

Atom	X	Y	Z
N1	-0.6918350	1.8273580	0.0000160
N2	-1.7955360	1.1548660	0.0000120
C3	0.3614070	0.9359020	-0.0000570
C4	-0.1596010	-0.3744240	-0.0001180
C5	0.6664740	-1.5088240	-0.0000640
H6	0.2643610	-2.5165630	-0.0001260
C7	2.0335420	-1.2734250	0.0000190
H8	2.7154420	-2.1185470	0.0000760
C9	2.5692660	0.0377940	0.0000650
H10	3.6474990	0.1631330	0.0001370
C11	1.7483590	1.1540590	0.0000260
H12	2.1477820	2.1625000	0.0000600
C13	-2.5843050	-1.1554070	0.0001150
H14	-2.5357890	-1.7868490	0.8926870
H15	-3.5226080	-0.6008450	-0.0005010
H16	-2.5352210	-1.7877600	-0.8917730
N17	-1.5115300	-0.1835260	-0.0000950

Table S2. B3LYP/6-311G(d,p) optimized geometry of MEBTA. The X, Y, and Z coordinates are in Å.

Atom	X	Y	Z
N1	-0.6906220	1.8238490	0.0000190
N2	-1.7903090	1.1536360	0.0000400
C3	0.3616100	0.9347540	-0.0000520
C4	-0.1595660	-0.3734950	-0.0000740
C5	0.6658940	-1.5057900	-0.0000120
H6	0.2654560	-2.5122910	-0.0000210
C7	2.0306940	-1.2719790	0.0000250
H8	2.7111940	-2.1158450	0.0000810
C9	2.5660980	0.0370160	0.0000230
H10	3.6424740	0.1621190	0.0000500
C11	1.7463270	1.1508720	-0.0000130
H12	2.1440730	2.1580520	0.0000020
C13	-2.5839950	-1.1537870	0.0000180
H14	-2.5353040	-1.7833190	0.8919140
H15	-3.5194190	-0.5976690	-0.0001380
H16	-2.5351790	-1.7834990	-0.8917460
N17	-1.5098780	-0.1822130	-0.0000080

Table S3. B3LYP/6-311+G(d,p) optimized geometry of MEBTA. The X, Y, and Z coordinates are in Å.

Atom	X	Y	Z
N1	-0.6882210	1.8249380	0.0000190
N2	-1.7895800	1.1557100	0.0000290
C3	0.3632500	0.9348150	-0.0000500
C4	-0.1608070	-0.3720210	-0.0000960
C5	0.6628750	-1.5062620	-0.0000300
H6	0.2611180	-2.5123020	-0.0000450
C7	2.0286020	-1.2743240	0.0000230
H8	2.7078770	-2.1191690	0.0000820
C9	2.5661960	0.0346600	0.0000360
H10	3.6428390	0.1577190	0.0000720
C11	1.7485230	1.1507920	0.0000030
H12	2.1499110	2.1566970	0.0000310
C13	-2.5838420	-1.1541850	0.0000550
H14	-2.5321380	-1.7827230	0.8923830
H15	-3.5227070	-0.6035160	-0.0003670
H16	-2.5317360	-1.7832780	-0.8918580
N17	-1.5113360	-0.1798310	-0.0000390

Table S4. BP86/6-31G(d,p) optimized geometry of MEBTA. The X, Y, and Z coordinates are in Å.

Atom	X	Y	Z
N1	-0.6945420	1.8415930	0.0000110
N2	-1.8112630	1.1643400	0.0000370
C3	0.3625350	0.9431180	-0.0000430
C4	-0.1604700	-0.3793890	-0.0000410
C5	0.6698870	-1.5180640	0.0000000
H6	0.2658280	-2.5345630	-0.0000270
C7	2.0463380	-1.2791270	0.0000200
H8	2.7340390	-2.1308850	0.0000570
C9	2.5826430	0.0382470	0.0000140
H10	3.6694850	0.1661000	0.0000390
C11	1.7558620	1.1622260	-0.0000170
H12	2.1580010	2.1790300	-0.0000240
C13	-2.5940440	-1.1651130	-0.0000070
H14	-2.5456610	-1.8017560	0.8994970
H15	-3.5385640	-0.6035500	0.0001850
H16	-2.5459020	-1.8014920	-0.8997120
N17	-1.5190130	-0.1894010	0.0000140

Table S5. BP86/6-311G(d,p) optimized geometry of MEBTA. The X, Y, and Z coordinates are in Å.

Atom	X	Y	Z
N1	-0.6930550	1.8377810	0.0000150
N2	-1.8057380	1.1630870	0.0000610
C3	0.3627400	0.9417620	-0.0000590
C4	-0.1603810	-0.3784810	-0.0000650
C5	0.6692690	-1.5147790	0.0000040
H6	0.2669800	-2.5301810	-0.0000030
C7	2.0432230	-1.2774130	0.0000320
H8	2.7296970	-2.1278870	0.0000940
C9	2.5790560	0.0374510	0.0000140
H10	3.6641380	0.1650170	0.0000310
C11	1.7535410	1.1588130	-0.0000300
H12	2.1538300	2.1745290	-0.0000270
C13	-2.5935390	-1.1631750	-0.0000210
H14	-2.5455090	-1.7974530	0.8991470
H15	-3.5348790	-0.5994710	0.0002410
H16	-2.5458380	-1.7970530	-0.8994970
N17	-1.5171870	-0.1883790	0.0000350

Table S6. BP86/6-311+G(d,p) optimized geometry of MEBTA. The X, Y, and Z coordinates are in Å.

Atom	X	Y	Z
N1	-0.6906010	1.8387730	0.0000390
N2	-1.8048880	1.1650710	0.0000770
C3	0.3644930	0.9417460	-0.0000990
C4	-0.1615290	-0.3769490	-0.0001370
C5	0.6662150	-1.5151430	-0.0000190
H6	0.2624930	-2.5301020	-0.0000500
C7	2.0409770	-1.2797000	0.0000490
H8	2.7262740	-2.1312130	0.0001510
C9	2.5789950	0.0350200	0.0000440
H10	3.6644330	0.1604670	0.0001020
C11	1.7557430	1.1586210	-0.0000280
H12	2.1597470	2.1730800	-0.0000040
C13	-2.5933350	-1.1633860	0.0000300
H14	-2.5423960	-1.7967120	0.8996530
H15	-3.5383180	-0.6054300	-0.0000950
H16	-2.5423330	-1.7968730	-0.8994740
N17	-1.5186920	-0.1859120	-0.0000200

Table S7. CAM-B3LYP/6-31G(d,p) optimized geometry of MEBTA. The X, Y, and Z coordinates are in Å.

Atom	X	Y	Z
N1	-0.6927010	1.8177170	0.0000140
N2	-1.7863920	1.1456340	0.0000050
C3	0.3589750	0.9305620	-0.0000380
C4	-0.1580700	-0.3698350	-0.0000970
C5	-0.6648320	-1.5029820	-0.0000460
H6	0.2611330	-2.5092100	-0.0000700
C7	2.0237910	-1.2688400	0.0000110
H8	2.7058540	-2.1127170	0.0000540
C9	2.5587700	0.0396240	0.0000470
H10	3.6361820	0.1640700	0.0000840
C11	1.7424340	1.1494980	0.0000260
H12	2.1402110	2.1577150	0.0000570
C13	-2.5731200	-1.1496510	0.0000940
H14	-2.5236560	-1.7795420	0.8919170
H15	-3.5109930	-0.5964440	-0.0004490
H16	-2.5231550	-1.7802910	-0.8911730
N17	-1.5053700	-0.1796140	-0.0000760

Table S8. CAM-B3LYP/6-311G(d,p) optimized geometry of MEBTA. The X, Y, and Z coordinates are in Å.

Atom	X	Y	Z
N1	-0.6915150	1.8143030	0.0000190
N2	-1.7812530	1.1444330	0.0000150
C3	0.3591350	0.9294850	-0.0000320
C4	-0.1580420	-0.3687760	-0.0000680
C5	0.6641240	-1.4999520	-0.0000220
H6	0.2620840	-2.5050530	-0.0000210
C7	2.0206840	-1.2674340	0.0000160
H8	2.7013730	-2.1101900	0.0000590
C9	2.5554530	0.0388400	0.0000240
H10	3.6311360	0.1630090	0.0000440
C11	1.7404250	1.1462900	0.0000030
H12	2.1366930	2.1532850	0.0000260
C13	-2.5723630	-1.1482280	0.0000430
H14	-2.5226290	-1.7760650	0.8914030
H15	-3.5075780	-0.5937220	-0.0002480
H16	-2.5223630	-1.7764650	-0.8910210
N17	-1.5036900	-0.1781850	-0.0000380

Table S9. CAM-B3LYP/6-311+G(d,p) optimized geometry of MEBTA. The X, Y, and Z coordinates are in Å.

Atom	X	Y	Z
N1	-0.6890360	1.8153960	0.0001100
N2	-1.7804620	1.1466440	0.0000740
C3	0.3608270	0.9294920	-0.0001060
C4	-0.1593450	-0.3672700	-0.0001830
C5	0.6610320	-1.5004130	-0.0000330
H6	0.2575550	-2.5050060	-0.0000500
C7	2.0184460	-1.2698150	0.0000680
H8	2.6979120	-2.1135650	0.0001930
C9	2.5554820	0.0364350	0.0000630
H10	3.6314600	0.1584220	0.0001230
C11	1.7426860	1.1461510	-0.0000280
H12	2.1426820	2.1518800	0.0000250
C13	-2.5721300	-1.1486290	0.0001310
H14	-2.5193670	-1.7751840	0.8921090
H15	-3.5110530	-0.5999470	-0.0007330
H16	-2.5186400	-1.7764760	-0.8908940
N17	-1.5051500	-0.1757310	-0.0002190

Table S10. Calculated maximum absorbance wavelength, λ (nm), and oscillator strength, f, in the UV-VIS spectra of MEBTA in the gas phase and in four solvents: EtOH, MeCN, DMSO, και Me_2CO, using B3LYP/6-311+G(d,p).

Gas phase	f	EtOH	f	MeCN	f	DMSO	f	Me_2CO	f
188.08	0.0047	184.78	0.0004	184.64	0.0014	184.60	0.0019	184.91	0.0001
188.75	0.0021	186.51	0.0041	186.45	0.0042	186.46	0.0041	186.55	0.0042
195.20	0	188.58	0.0023	188.42	0.0029	188.36	0.0039	188.68	0.0019
197.65	0.0111	188.92	0.0253	188.77	0.0247	188.73	0.0245	189.02	0.0258
198.17	0.0621	189.11	0.5442	189.04	0.5279	189.48	0.6150	189.08	0.5384
198.38	0.0027	200.75	0.0621	200.78	0.0588	200.86	0.0671	200.71	0.0628
212.95	0.0074	202.31	0.0033	202.15	0.0031	202.13	0.0031	202.41	0.0033
235.93	0.0848	239.64	0.0064	239.36	0.0064	239.29	0.0066	239.78	0.1326
251.50	0.0047	239.84	0.1330	239.84	0.1315	240.13	0.1386	239.82	0.0065
255.63	0.0872	256.75	0.1261	256.67	0.1251	256.98	0.1305	256.74	0.1258

Table S11. Calculated maximum absorbance wavelength, λ (nm), and oscillator strength, f, in the UV-VIS spectra of MEBTA in the gas phase and in 4 solvents: EtOH, MeCN, DMSO, και Me_2CO, using BP86/6-311+G(d,p).

Gas phase	f	EtOH	f	MeCN	f	DMSO	f	Me_2CO	f
201.08	0.0074	191.27	0.0090	191.08	0.0089	190.99	0.0090	191.40	0.0090
201.34	0	194.56	1.0344	194.34	1.0311	195.06	1.0386	194.56	1.0342
201.80	0.0011	202.34	0.1671	202.33	0.1609	202.53	0.1943	202.32	0.1653
211.42	0.0009	203.04	0.0037	202.83	0.0035	202.76	0.0036	203.17	0.0037
215.95	0.0068	207.23	0.0021	207.13	0.0021	207.12	0.0022	207.29	0.0021
225.50	0.0151	216.31	0	216.02	0	215.87	0	216.50	0
229.67	0	228.20	0.0137	228.24	0.0134	228.29	0.0143	228.16	0.0137
252.09	0.0501	255.70	0.0840	255.71	0.0830	255.95	0.0880	255.65	0.0838
275.88	0.0719	270.28	0.0027	269.90	0.0027	269.75	0.0028	270.53	0.0027
286.87	0.0019	278.10	0.1011	278.05	0.1002	278.38	0.1042	278.07	0.1008

Table S12. Calculated maximum absorbance wavelength, λ (nm), and oscillator strength, f, in the UV-VIS spectra of MEBTA in the gas phase and in 4 solvents: EtOH, MeCN, DMSO, και Me_2CO, using CAM-B3LYP/6-311+G(d,p).

CAM-B3LYP	f	EtOH	f	MeCN	f	DMSO	f	Me_2CO	f
175.94	0.4323	172.91	0.3350	172.89	0.3445	173.08	0.3275	172.89	0.3329
176.68	0.0012	174.89	0.0053	174.79	0.0071	174.76	0.0091	174.95	0.0034
176.95	0.0053	175.15	0.0239	175.08	0.0219	175.09	0.0205	175.20	0.0258
177.21	0.5829	176.46	0.1399	176.44	0.1326	176.60	0.1409	176.45	0.1429
181.55	0.0155	178.32	0.0141	178.24	0.0138	178.27	0.0141	178.37	0.0143
183.38	0.0130	181.13	1.1192	180.97	1.1030	181.65	1.1567	181.10	1.1185
196.35	0.0078	190.31	0.0027	190.23	0.0026	190.27	0.0026	190.36	0.0028
222.06	0.1181	223.99	0.0106	223.77	0.0106	223.75	0.0108	224.13	0.0106
233.29	0.0083	225.84	0.1826	225.81	0.1807	226.14	0.1895	225.79	0.1821
240.41	0.0922	240.29	0.1346	240.17	0.1333	240.44	0.1398	240.31	0.1343

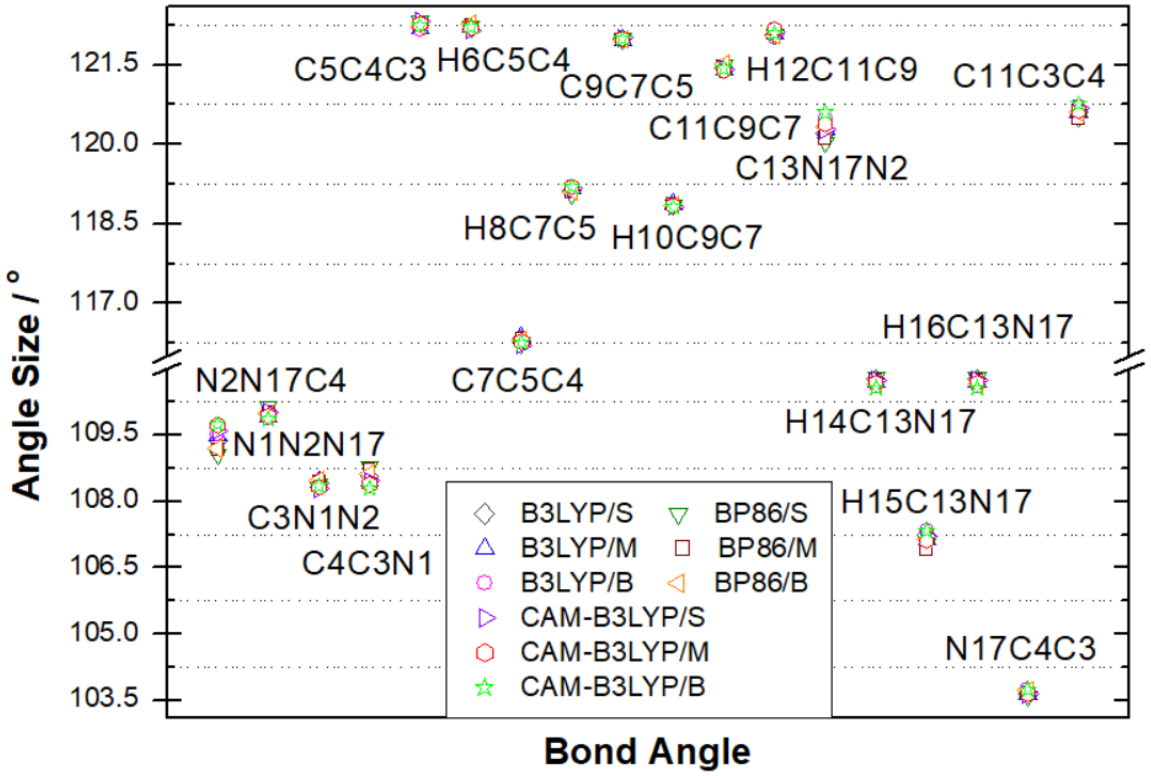


Fig. S1. (Color online) Calculated bond angles (in degrees, °) of MEBTA. The DFT functionals are shown in the inset. The S, M, και B symbols represent the 6-31G(d,p), 6-311G(d,p), και 6-311+G(d,p) basis sets, respectively. The Y-axis is not drawn continuously, and the scale is different before and after the break.

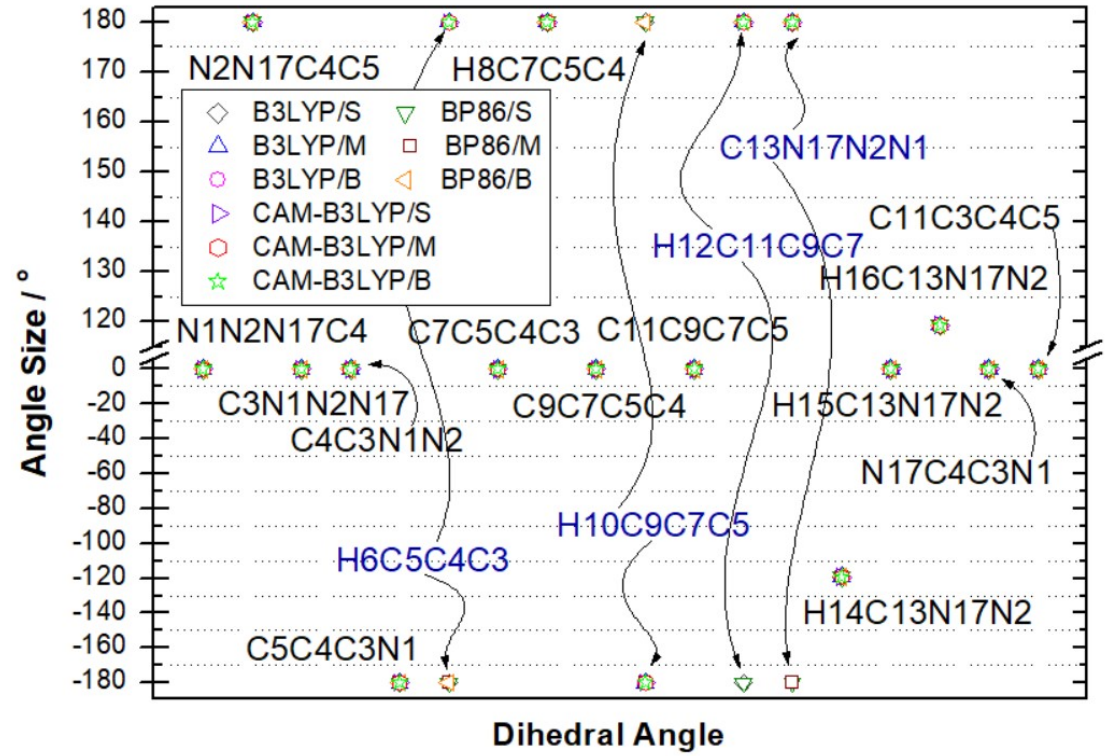
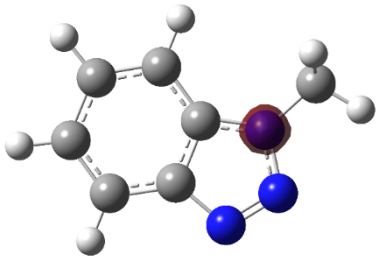


Fig. S2. (Color online) Calculated dihedral angles (°) of MEBTA. The DFT functionals are shown in the inset. The S, M, and B symbols represent the 6-31G(d,p), 6-311G(d,p), and 6-311+G(d,p) basis sets, respectively. The Y-axis is not drawn continuously, and the scale is different before and after the break. The angles in blue approach ±180° and are shown twice in the upper and lower part of the diagram.

In Fig. S2, we observe that results from the different functionals look similar except for four dihedral angles: H6C5C4C3, H10C9C7C5, H12C11C9C7, and C13N17N2N1 which are shown in blue color. For those four angles, the differing functionals give different signs for the angle values, and for this reason, they are plotted in two different parts across the Y-axis. Among these values, the CAM-B3LYP functionals converge with increasing basis set size (the values overlap in the figure), but this convergence does not appear for all the rest functionals.

The dihedral angles of the carbon atoms in the benzene ring (C7C5C4C3, C9C7C5C4, C11C9C7C5, and C11C3C4C5) tend to 0°, but those involving the hydrogens (H6C5C4C3, H8C7C5C4, H10C9C7C5, and H12C11C9C7) tend to ±180°, which is consistent with the expected benzene ring planar geometry. The values of the dihedral angles of the triazole ring (N1N2N17C4, C3N1N2N17, C4C3N1N2, και N17C4C3N1) tend to 0°, indicating that the triazole ring adopts a planar geometry too. Taking into account that the dihedral angles which connect the two rings (N2N17C4C5, C5C4C3N1) take the value of 180°, we conclude that the two rings are on the same plane. This will be consistent with the N1=N2 being a double bond and with its electronic cloud delocalization through the N1-C3 towards the benzene ring. Also, because of the planar geometry of the triazole ring, the N17 atom may participate in the delocalization of its electronic density towards the benzene ring through its neighboring atoms (N2, C4) as it has a lone pair of electrons and it is connected with a methyl group which may offer some electronic density.

The value of the C13N17N2N1 dihedral angle tends to 180°, something which indicates that the carbon atom of the methyl group is in the same plane with the rings, and therefore, the N17 takes an almost planar triangular geometry instead of the expected tetrahedral, with the non-bonding electron pair perpendicular to the plane of the ring in order to participate in the delocalization. Also, the value of the H15C13N17N2 dihedral angle tends to 0°, which is in agreement with the assumption that the H15 is attracted by the N2 lone pair of electrons (which lies in the same plane with the two rings as N2 is sp^2 hybridized).



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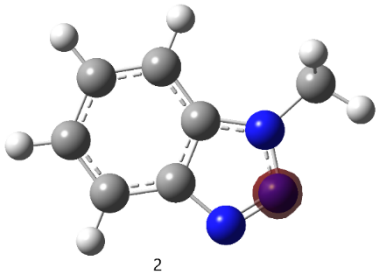

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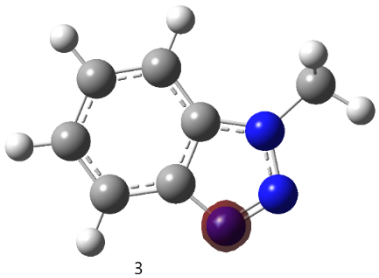

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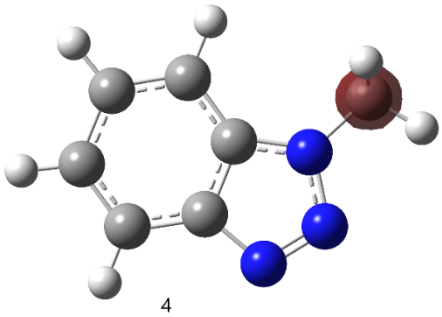

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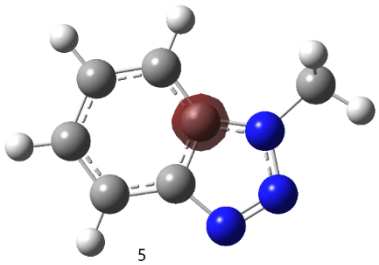

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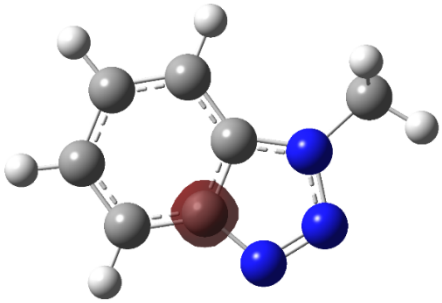

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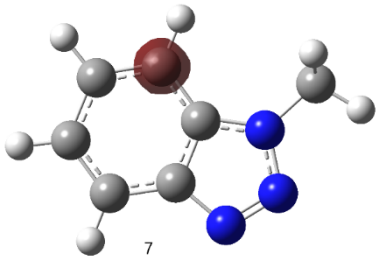

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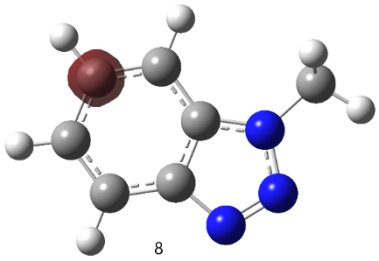

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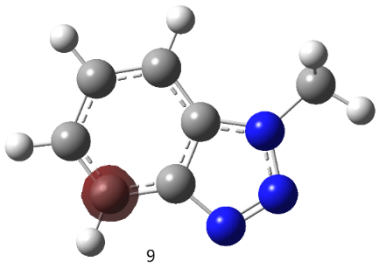

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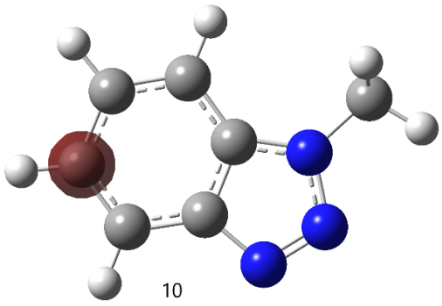

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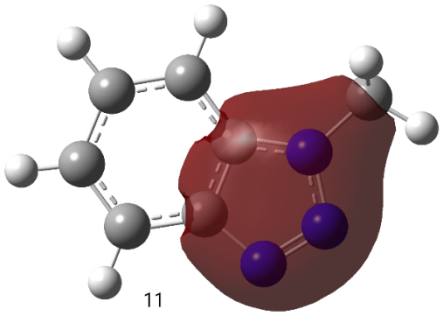

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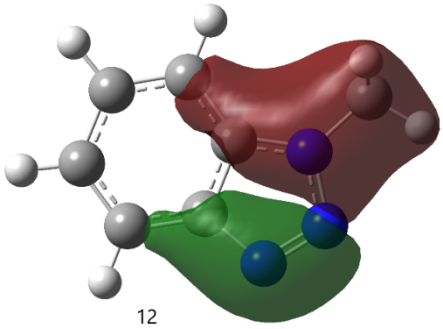

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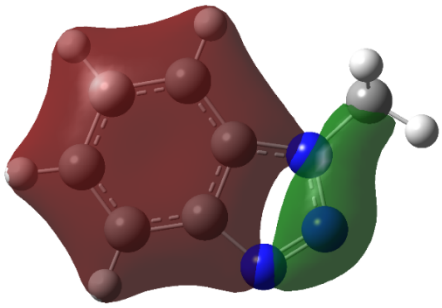

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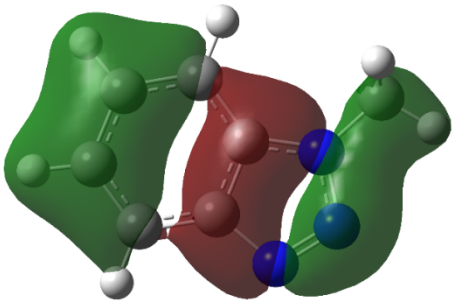

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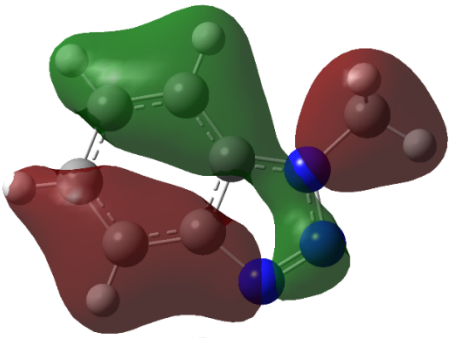

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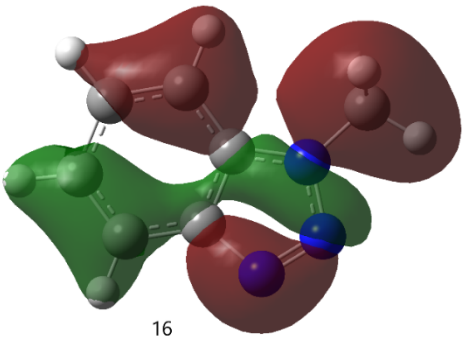

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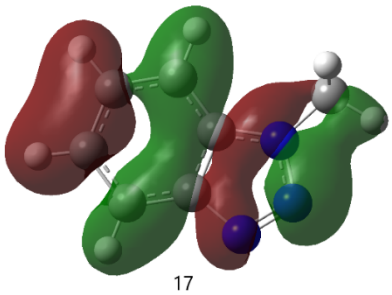

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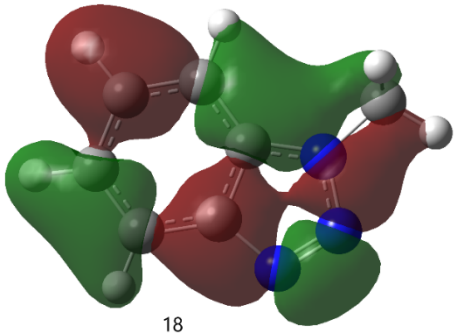

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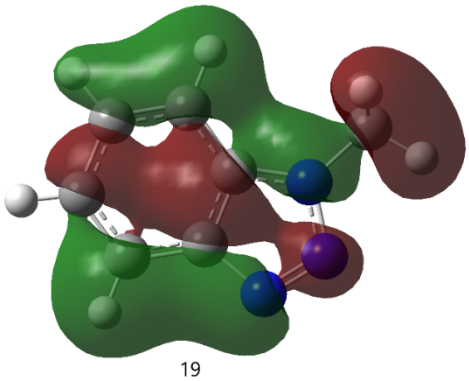

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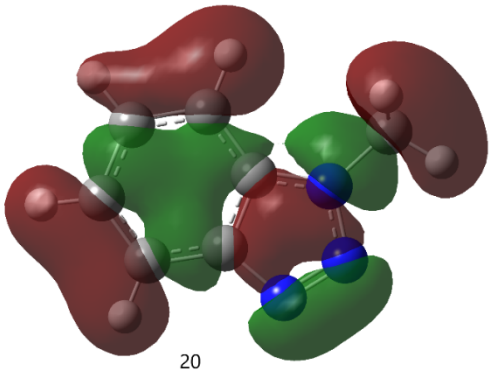

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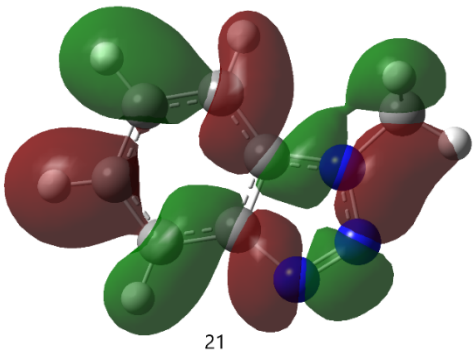

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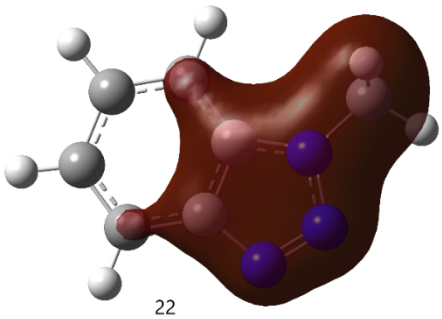

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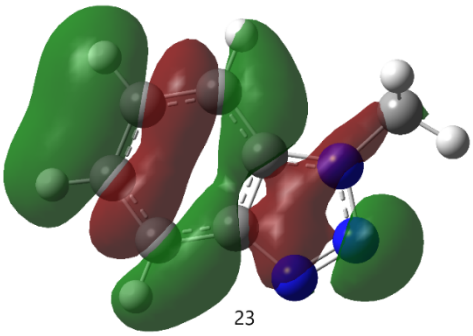

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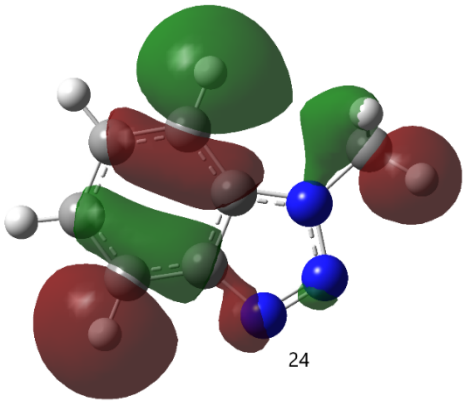

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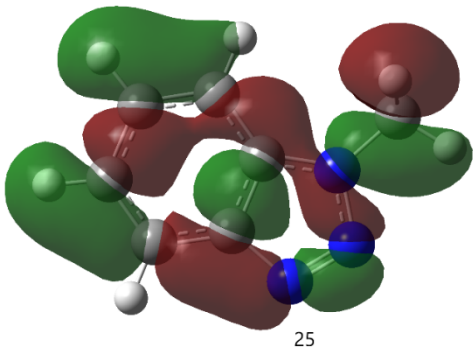

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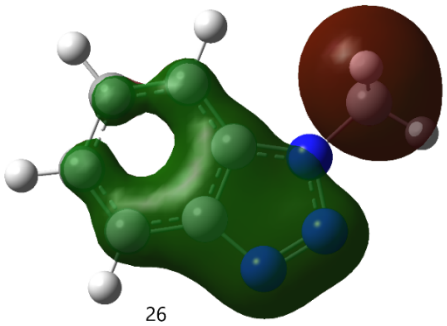

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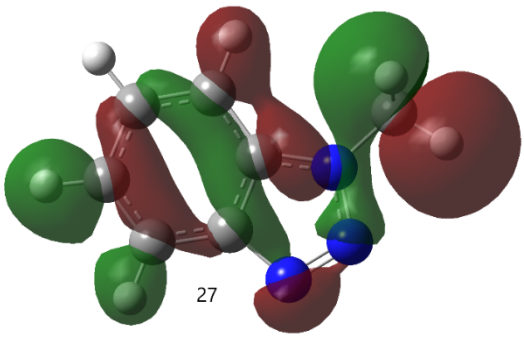

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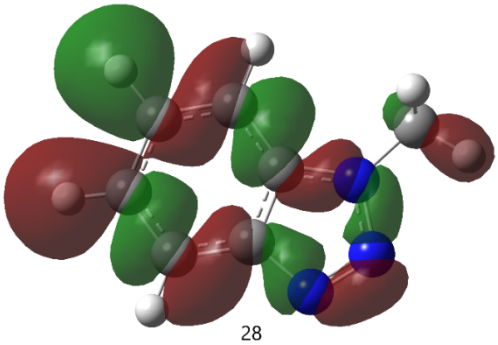

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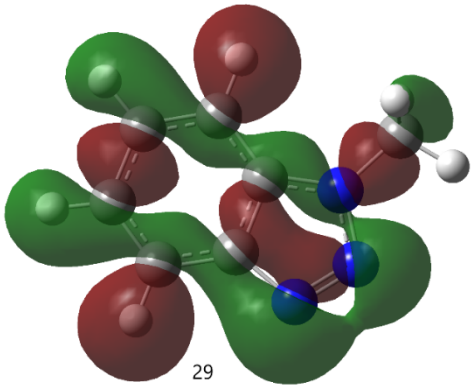

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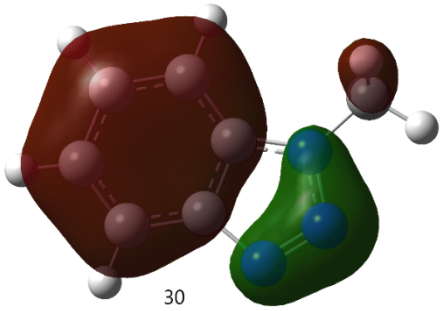

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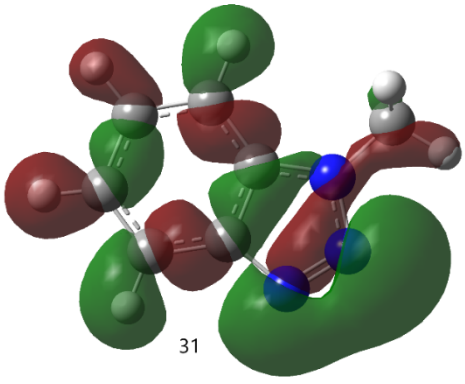

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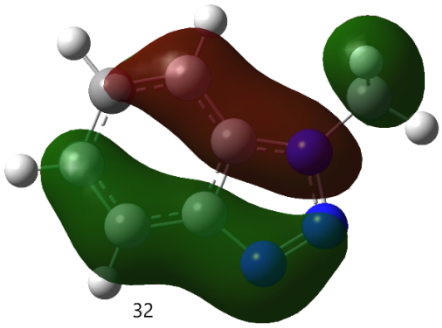

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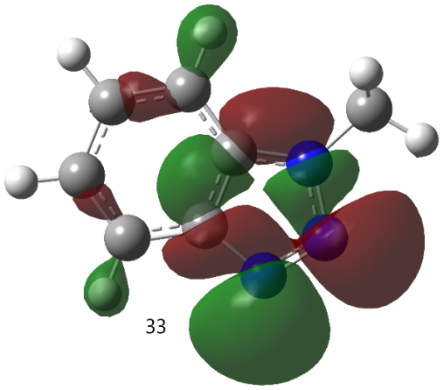

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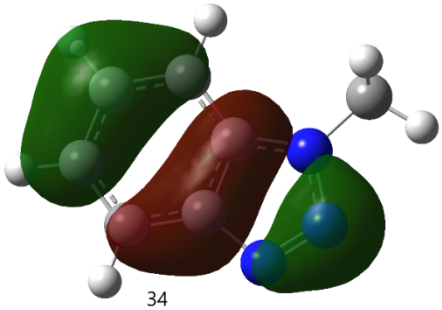

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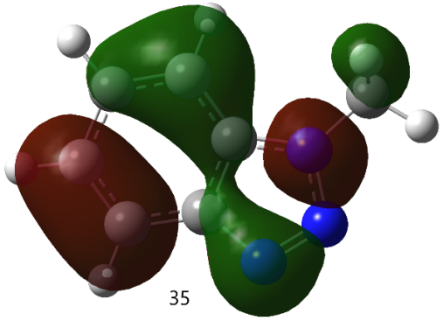

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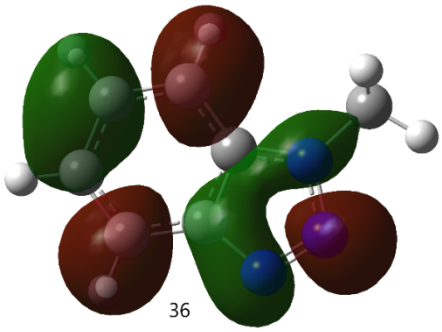

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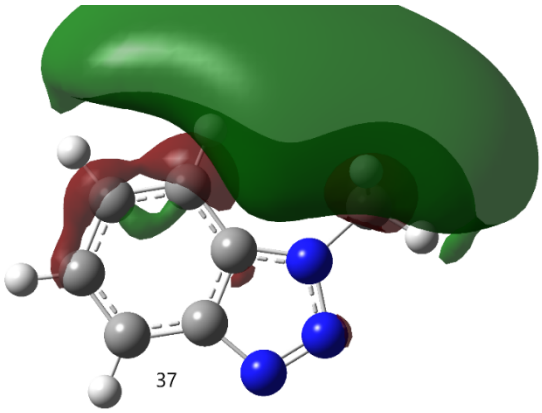

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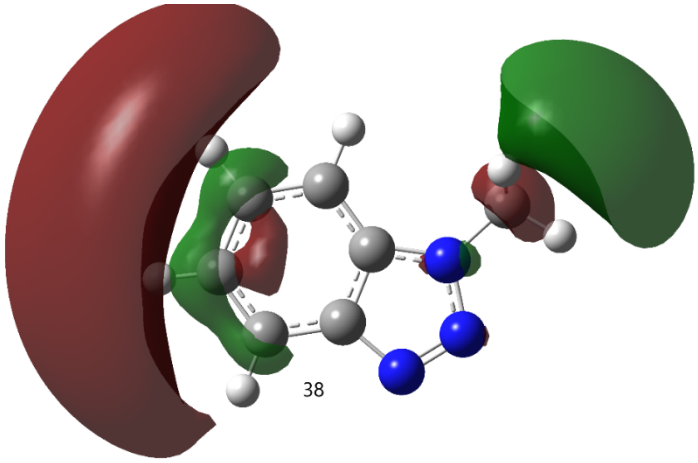

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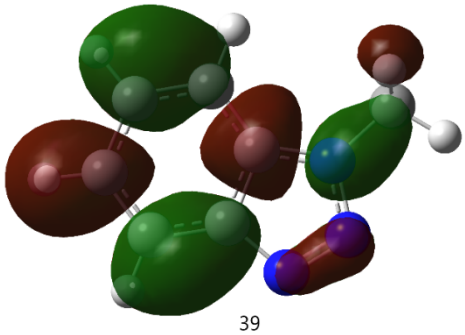

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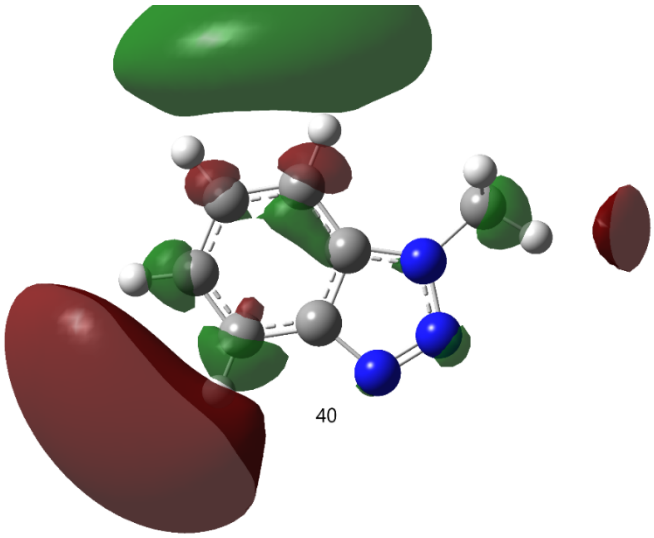

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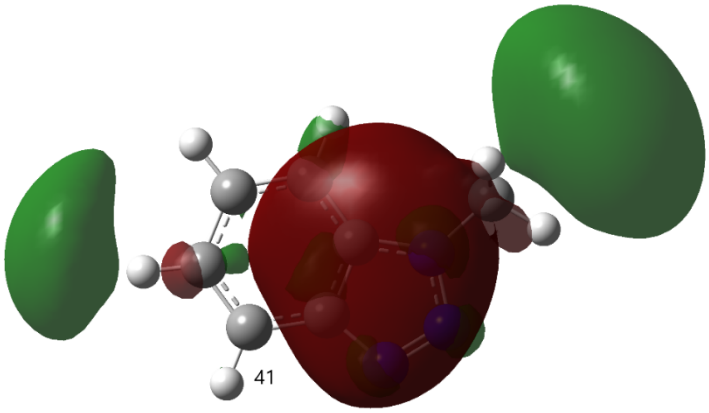
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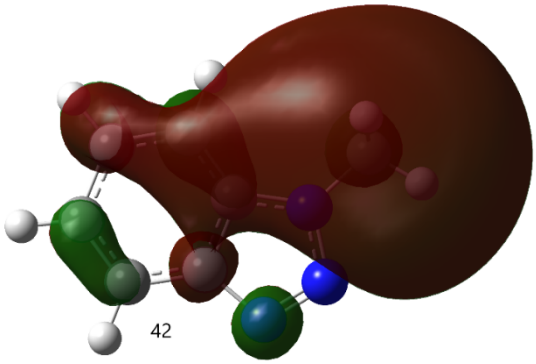
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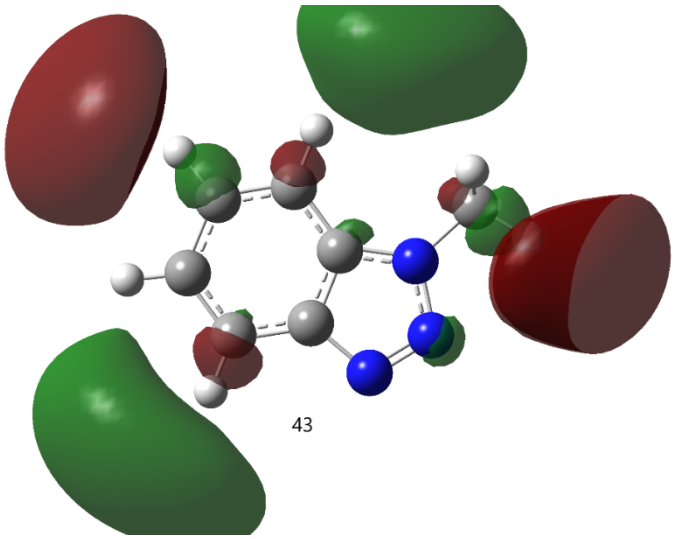
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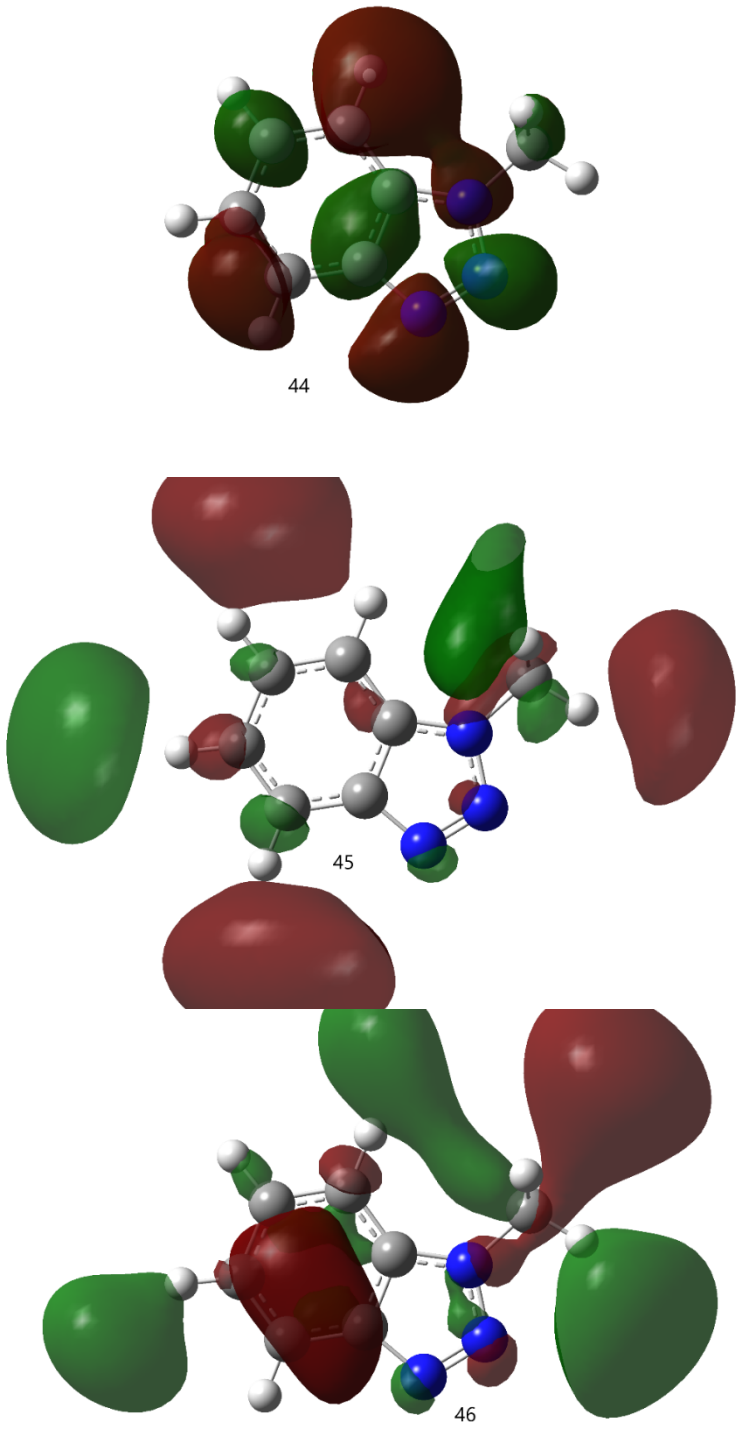

Fig. S3. (Color online) The first 46 lowest molecular orbitals of MEBTA obtained using CAM-B3LYP/6-311+G(d,p) level of theory.