ARTICLE

Electronic Supplementary Information

Calculation of magnetic response properties of tetrazines†

Received date
Accepted date

DOI: 10.1039/x0xx00000x

Mesías Orozco-Ic,[a] Christian A. Celaya [a,b] and Dage Sundholm [a,*]

The Table S1 contains the geometrical data as well as the value of the HOMO-LUMO gap of the studied structures. The labels of the bond lengths are referenced are shown in Figure 1 of the main text. Table S2 shows the values of the current strengths computed in different planes that intersect the corresponding different bonds of the other tetrazine isomers. In the Table 1 of the main text, the reported current strengths were integrated in the A plane. Table S3 contains the orbital contributions to B_z^{ind} for the other tetrazine isomers computed in the ring centers. Figure S1 – S7 are the magnetic responses of the studied molecules. Finally, the Cartesian coordinates computed at the PBE0-D3/def2-TZVP level are also provided.

[a] *Department of Chemistry, University of Helsinki, P.O. Box 55, A. I. Virtasen aukio 1, FIN-00014 Helsinki, Finland. E-mail: dage.sundholm@helsinki.fi*
[b] *Departamento de Materiales de Baja Dimensionalidad, Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, Ciudad de México 04510, México.*

Table S1. Symmetry, bond lengths (in Å) and HOMO-LUMO gaps (in eV) of the studied molecules calculated at the PBE0-D3/def2-TZVP level.

Molecule	Symmetry	r_A	r_B	r_C	HOMO-LUMO
Benzene	D_{6h}	1.39	-	-	7.11
1,2,3,5-tetrazine	C_{2v}	1.32	1.33	1.30	4.85
4,6-dimethyl-1,2,3,5-tetrazine	C_{2v}	1.33	1.34	1.31	4.78
4,6-bis(1-methylethenyl)-1,2,3,5-tetrazine	C_{2v}	1.32	1.34	1.30	4.38
4,6-diphenyl-1,2,3,5-tetrazine	C_{2v}	1.33	1.34	1.30	4.56
4,6-[1,2,3,5]-ditetrazinyl-1,2,3,5-tetrazine	C_s	1.32	1.33	1.30	4.04

Table S2. Diatropic, paratropic and net current strengths (in nA/T) calculated at the PBE0/def2-SVP level for the tetrazine ring of the two other isomers. The ring-current strengths are obtained by integrating the current density in planes that intersect different bonds of the ring. The net current strength is practically independent of the chosen bond showing that the charge conservation condition is almost fulfilled also when using the def2-SVP basis sets. Replacing CH with N breaks the C_6 symmetry of benzene, which may lead to nonvertical current-density vortices that affect the accuracy of the numerical integration, because some current strength contributions may be omitted or considered twice with opposite sign.

Structure	Plane	Diatropic	Paratropic	Net
1,2,3,4-tetrazine	A	13.59	-3.88	9.70
	B	16.95	-6.78	10.17
	C	15.63	-5.48	10.14
	D	16.48	-6.45	10.03
1,2,4,5-tetrazine	A	17.45	-7.30	10.15
	B	14.91	-4.99	9.92

Table S3. Orbital contributions to the $B_z^{ind}(0)$ values (in ppm) for the other tetrazine isomers calculated in the center of the ring at the PBE0/def2-SVP level.

Structure	core+σ	π	total
1,2,3,4-tetrazine	30.14	-37.03	-6.89
1,2,4,5-tetrazine	30.35	-37.29	-6.94

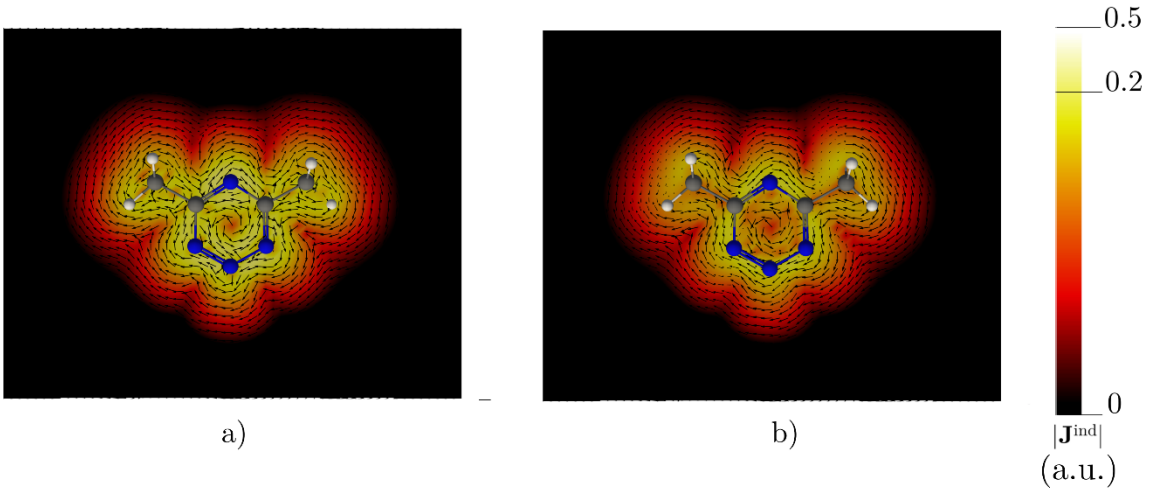

Figure S1. $\mathbf{J}^{ind}$ plots calculated at a) 0 bohr and b) 1 bohr away from the molecular plane of 4,6-dimethyl-1,2,3,5-tetrazine. The arrows show the direction of $\mathbf{J}^{ind}$, while the color contours indicate its magnitude. $|\mathbf{J}^{ind}|$ values are given in atomic units (1 a.u. = 100.63 nA/T/Å^2). The figure was made with ParaView.

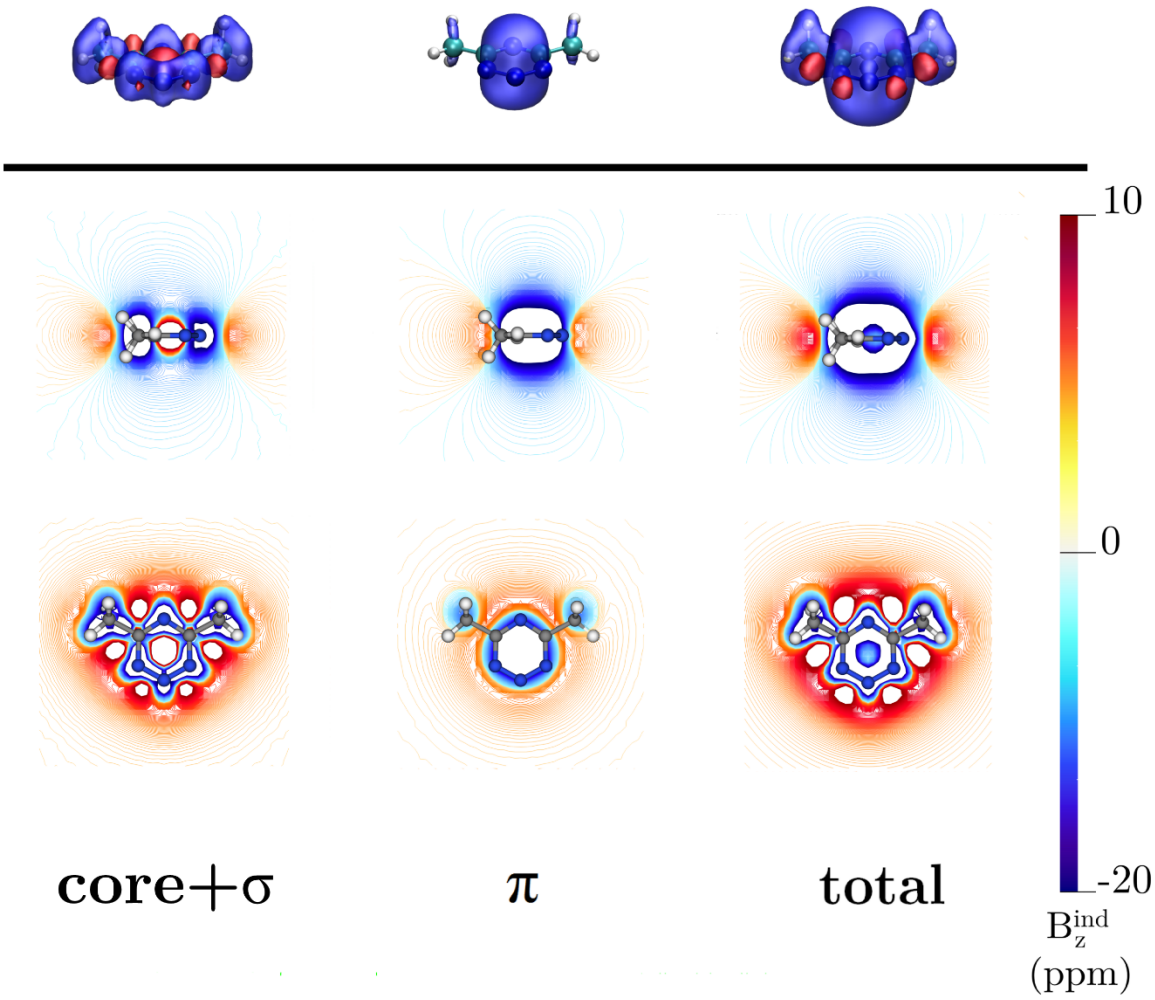

Figure S2. The isosurfaces of the B_z^{ind} of 4,6-dimethyl-1,2,3,5-tetrazine are shown in the upper panel. The shielding and deshielding cones at -10 ppm and 10 ppm are in blue and red, respectively. The B_z^{ind} isolines calculated in the transverse and molecular planes are shown in the lower panel. The figure was made with VisIt.

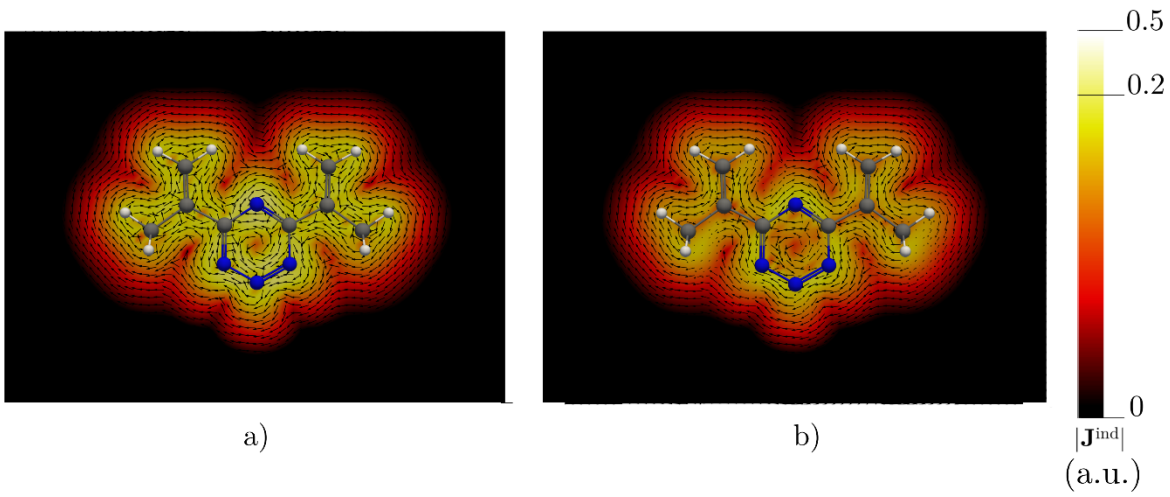

Figure S3. $\mathbf{J}^{ind}$ plots calculated at a) 0 bohr and b) 1 bohr from the molecular plane of 4,6-bis(1-methylethenyl)-1,2,3,5-tetrazine. The arrows show the direction of $\mathbf{J}^{ind}$, while the color indicates its strength. $|\mathbf{J}^{ind}|$ values are given in atomic units (1 a.u. = 100.63 nA/T/Å^2). The figure was made with ParaView.

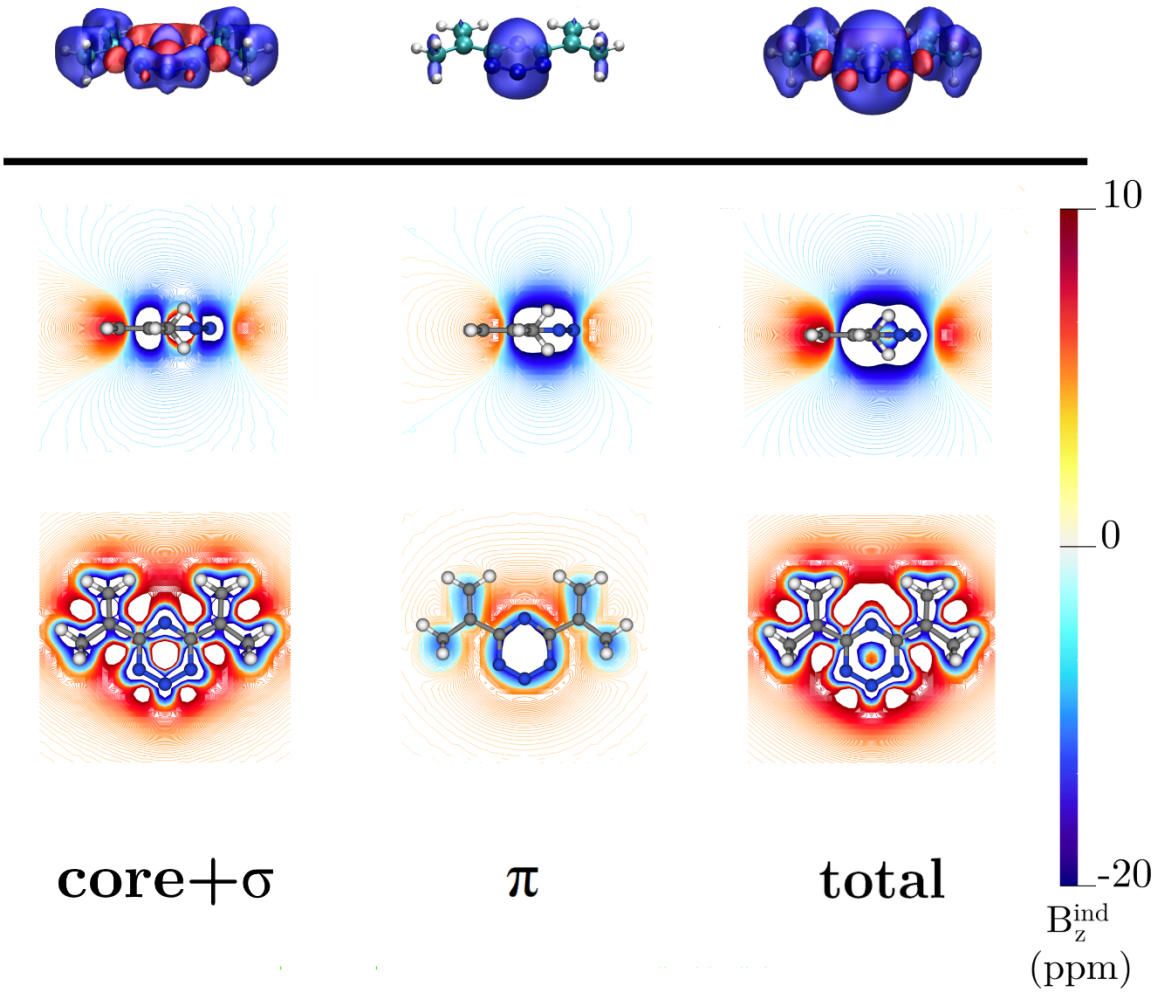

Figure S4. The isosurfaces of the B_z^{ind} of 4,6-bis(1-methylethenyl)-1,2,3,5-tetrazine are shown in the upper panel. The shielding and deshielding cones at -10 ppm and 10 ppm are in blue and red, respectively. The B_z^{ind} isolines calculated in the transverse and molecular planes are shown in the lower panel. The figure was made with VisIt.

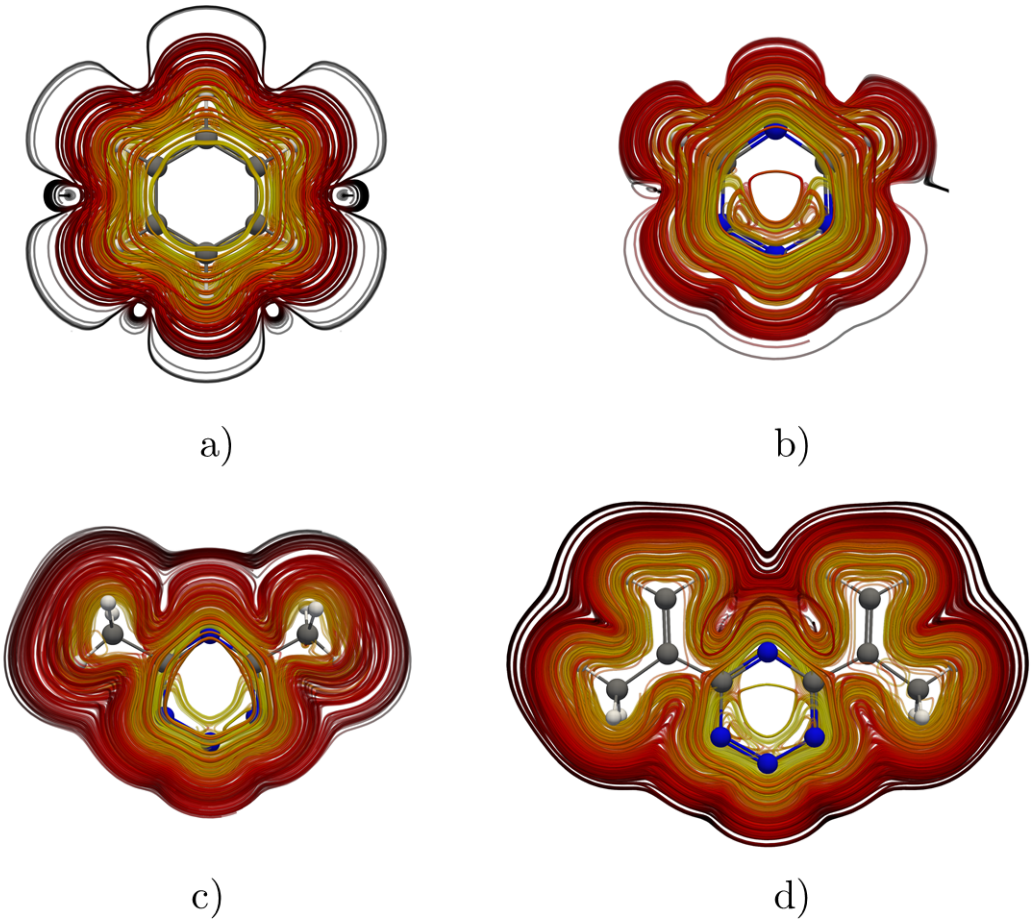

Figure S5. Streamlines representation of $\mathbf{J}^{ind}$ for a) benzene, b) 1,2,3,5-tetrazine, c) 4,6-dimethyl-1,2,3,5-tetrazine, and d) 4,6-di-isopropyl-1,2,3,5-tetrazine. The figure was made with ParaView.

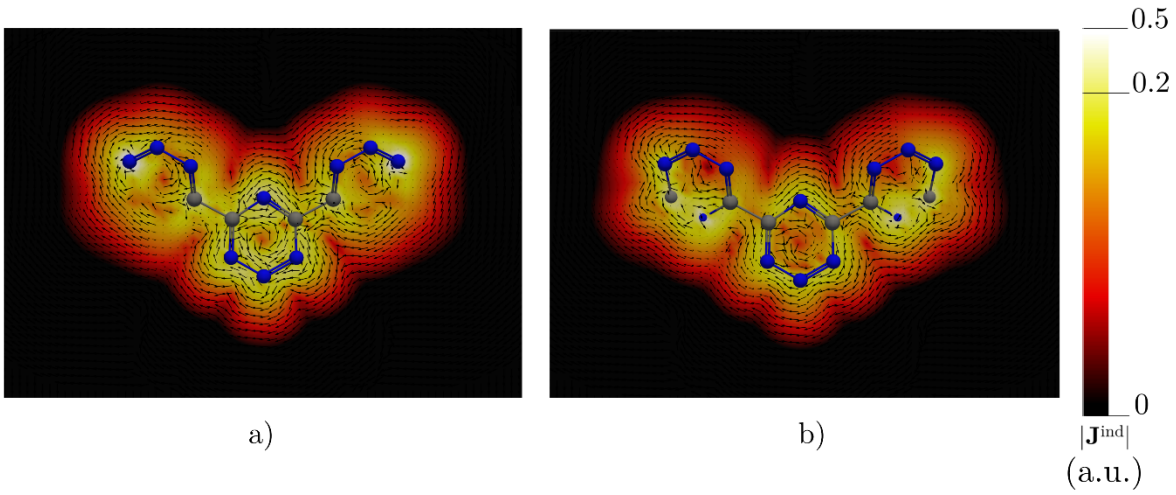

Figure S6. $\mathbf{J}^{ind}$ plots calculated at a) 0 bohr and b) 1 bohr from the molecular plane of 4,6-[1,2,3,5]-ditetrazinyl-1,2,3,5-tetrazine. The arrows show the direction of $\mathbf{J}^{ind}$, while the color indicates its strength. $|\mathbf{J}^{ind}|$ values are given in atomic units (1 a.u. = 100.63 nA/T/Å^2). The figure was made with ParaView.

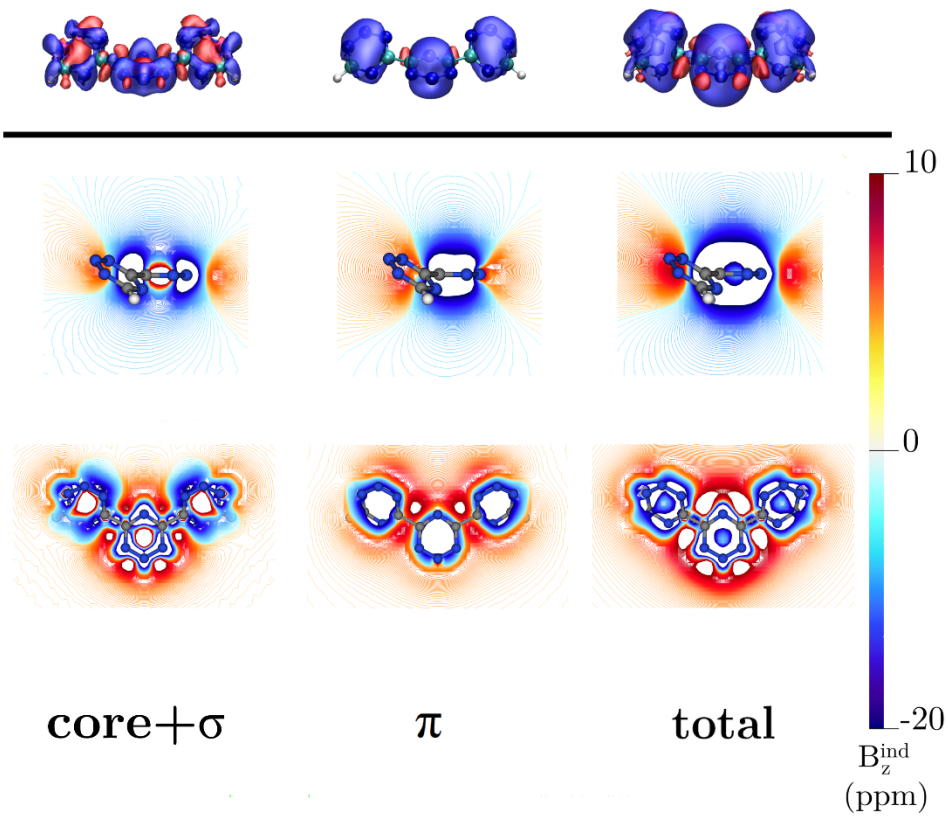

Figure S7. The isosurfaces of the B_z^{ind} of 4,6-[1,2,3,5]-ditetrazinyl-1,2,3,5-tetrazine are shown in the upper panel The shielding and deshielding cones at -10 ppm and 10 ppm are in blue and

red, respectively. The B_z^{ind} isolines calculated in the transverse and molecular planes are shown in the lower panel. The figure was made with VisIt.

Cartesian coordinates of the studied molecules computed at PBE0-D3/def2-TZVP level.

Benzene

C	1.201995494	0.693972422	0.000000000
C	0.000000000	1.387944844	0.000000000
C	-1.201995494	0.693972422	0.000000000
C	-1.201995494	-0.693972422	0.000000000
C	0.000000000	-1.387944844	0.000000000
C	1.201995494	-0.693972422	0.000000000
H	2.140987581	1.236099756	0.000000000
H	0.000000000	2.472199512	0.000000000
H	-2.140987581	1.236099756	0.000000000
H	-2.140987581	-1.236099756	0.000000000
H	0.000000000	-2.472199512	0.000000000
H	2.140987581	-1.236099756	0.000000000

1,2,3,5-tetrazine

C	-0.654242566	1.098455000	0.000000000
C	-0.654242566	-1.098455000	0.000000000
N	0.676073434	1.137045000	0.000000000
N	1.324726434	0.000000000	0.000000000
N	0.676073434	-1.137045000	0.000000000
N	-1.388466566	0.000000000	0.000000000
H	-1.160830566	-2.059712000	0.000000000
H	-1.160830566	2.059712000	0.000000000

4,6-dimethyl-1,2,3,5-tetrazine

C	1.113676321	-0.297153258	0.002817545
C	-1.113677253	-0.297149945	-0.002843255
N	1.137696121	1.041703741	0.004256551
N	0.000004329	1.683329899	0.000006319
N	-1.137700655	1.041702057	-0.004258077
N	0.000000928	-1.015163101	-0.000018831
C	2.419730527	-1.006230452	-0.001483817
H	2.525066019	-1.570755794	-0.931379322
H	3.239893677	-0.297385441	0.088959817
H	2.451670925	-1.728364290	0.816624874
C	-2.419729644	-1.006231751	0.001507130
H	-2.525224198	-1.570338409	0.931643311
H	-3.239883757	-0.297426762	-0.089339530
H	-2.451532118	-1.728722912	-0.816285558

4,6-bis(1-methylethenyl)-1,2,3,5-tetrazine

C	1.115622123	-0.075823767	-0.000008081
C	-1.115629877	-0.075840756	0.000019084
N	1.136142114	-1.419747777	0.000007709
N	0.000011110	-2.060173771	-0.000017755
N	-1.136147886	-1.419742759	-0.000029176
N	0.000001127	0.636975243	0.000004776
C	-2.426091873	0.601113257	0.000012607
C	2.426090127	0.601115230	-0.000005232
C	-2.472825865	1.933366263	0.000039452
H	-1.565498861	2.523732257	0.000073918
C	2.472834135	1.933368245	-0.000071267
H	1.565512139	2.523741258	-0.000102105
H	3.422174139	2.455655242	-0.000064510
H	-3.422161862	2.455660270	0.000055799
C	3.644745121	-0.264132791	0.000058659
H	3.657810009	-0.921311291	0.872665749
H	3.657913225	-0.921285297	-0.872567259
H	4.547360125	0.347063201	0.000120495
C	-3.644751879	-0.264126738	-0.000014596
H	-3.657865775	-0.921268243	-0.872649547
H	-3.657873991	-0.921316237	0.872583459
H	-4.547363875	0.347072270	-0.000002053

4,6-diphenyl-1,2,3,5-tetrazine

C	4.8178463629	0.0386006579	0.0000000000
C	3.6021652739	0.6996617058	0.0000000000
C	2.4118781840	-0.0285683471	0.0000000000
C	2.4566951841	-1.4225694538	0.0000000000
C	3.6750062788	-2.0780685030	0.0000000000
C	4.8571173686	-1.3492744466	0.0000000000
H	5.7399684160	0.6080317019	0.0000000000
H	3.5561082686	1.7810297879	0.0000000000
H	1.5278051128	-1.9784874944	0.0000000000
H	3.7047232802	-3.1614725840	0.0000000000
H	5.8111014272	-1.8644964867	0.0000000000
C	-3.6021652739	0.6996617058	0.0000000000
C	-4.8178463629	0.0386006579	0.0000000000
C	-4.8571173686	-1.3492744466	0.0000000000
C	-3.6750062788	-2.0780685030	0.0000000000
C	-2.4566951841	-1.4225694538	0.0000000000
C	-2.4118781840	-0.0285683471	0.0000000000
H	-3.5561082686	1.7810297879	0.0000000000
H	-5.7399684160	0.6080317019	0.0000000000
H	-5.8111014272	-1.8644964867	0.0000000000
H	-3.7047232802	-3.1614725840	0.0000000000
H	-1.5278051128	-1.9784874944	0.0000000000
C	-1.1167320821	0.6664037042	0.0000000000

C	1.1167320821	0.6664037042	0.0000000000
N	-1.1360900844	2.0089608066	0.0000000000
N	0.0000000000	2.6478738533	0.0000000000
N	1.1360900844	2.0089608066	0.0000000000
N	0.0000000000	-0.0476343486	0.0000000000

4,6-[1,2,3,5]-ditetrazinyl-1,2,3,5-tetrazine

C	-0.887374677	4.498844000	-0.680886521
N	-0.173333544	3.389555000	-0.735754035
C	-0.699355114	2.414103000	-0.015706263
N	-1.809771915	2.502766000	0.712445762
N	-2.443962584	3.647413000	0.726281488
N	-2.003920708	4.661296000	0.025219729
N	-0.173333544	-3.389549000	-0.735754035
C	-0.887374677	-4.498838000	-0.680886521
N	-2.003920708	-4.661290000	0.025219729
N	-2.443962584	-3.647407000	0.726281488
N	-1.809771915	-2.502760000	0.712445762
C	-0.699355114	-2.414097000	-0.015706263
C	0.000000000	-1.098734000	0.000000000
C	0.000000000	1.098740000	0.000000000
N	1.331818107	-1.136177000	-0.016180554
N	1.978917480	0.000003000	0.000000000
N	1.331818107	1.136183000	-0.016180554
N	-0.732079427	0.000003000	0.033759539
H	-0.548170035	5.357726000	-1.251633427
H	-0.548170035	-5.357720000	-1.251633427