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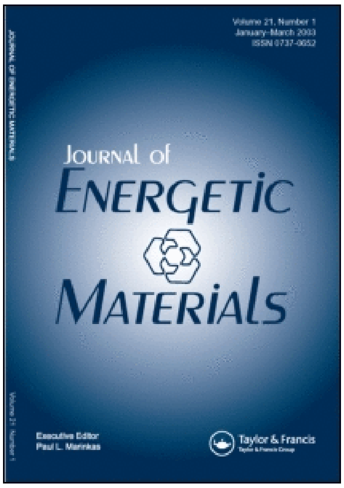

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

DFT calculations of the thermochemistry and structures of tetrazine derivatives

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To cite this Article Wilcox, Charles F. , Zhang, Yi-Xue and Bauer, S. H.(2002) 'DFT calculations of the thermochemistry and structures of tetrazine derivatives', Journal of Energetic Materials, 20: 1, 71 — 92

To link to this Article: DOI: 10.1080/07370650208244815

URL: http://dx.doi.org/10.1080/07370650208244815

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DFT CALCULATIONS OF THE THERMOCHEMISTRY AND STRUCTURES OF TETRAZINE DERIVATIVES

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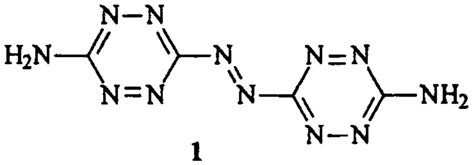
ABSTRACT

Enthalpies of formation and standard state entropies were calculated for tetrazine, amino- and nitrotetrazines, and four extended ditetrazines using DFT programs. The derived values were corrected with the previously derived supplementary set of four parameters. The basic geometric structural features of the minimum energy states of the tetrazines are summarized.

Journal of Energetic Materials Vol. 20, 071-092 (2002)
Published in 2002 by Dowden, Brodman & Devine, Inc.

INTRODUCTION

Tetrazine-based energetic materials comprise an interesting class of explosives for which imaginative synthetic routes have been developed recently[1]. The tetrazines (e.g., 1) have unique features.



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They derive a substantial fraction of their explosive power from their high heats of formation rather than from oxidation of their carbon content. This is significant, since rapid high gas generation occurs early in their decomposition, in contrast to the high exoergicities of CH/NO_2 formulations that appear after an initial pyrolysis and subsequent oxidations. In addition, the tetrazine based compounds have relatively high densities, are generally insensitive to impact and can be readily formulated for good oxygen balance. They provide useful explosives and smokeless pyrotechnics.

High nitrogen content compounds present a challenging group of molecular species for calculation of their thermochemical parameters. Politzer and co-workers[2] developed several computationally efficient *ab initio* and DFT models for this group of compounds, and auxiliary computational tools for converting

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calculated gas-phase heats of formation into condensed-phase heats of formation. Williams and Whitehead[3] published an extensive compilation of heats of formation of azole, azines and benzazoles, derived *via* semi-empirical and *ab initio* computations. They found that PM3 performs well on azoles and benzazoles, but underestimates the heats of formation of azines. However, they developed a set of correction terms that brought the semiempirical azine enthalpies into agreement with the experimental values. For their ab initio calculations they utilized 4-31G and 6-31G** basis sets. More recently, Rice and co-workers[4] applied the B3LYP/6-31G* DFT method to 32 high-energy nitrogen compounds and report an rms fit to the experimental data of 3.1 kcal/mol.

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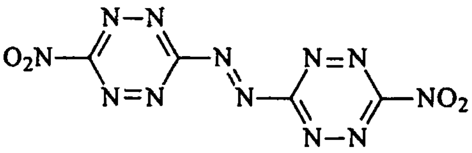
As part of our study of the gas phase pyrolysis of TNAZ (1,3,3-trinitroazetidine)[5], representative of the "new generation" of explosives, we developed a computational model[6] that could be used to estimate the energies of both the singlet and the radical species generated during their initial decompositions, and to offer insights into the structural bases for those energies. That model, while based on procedures developed by other workers,[2,4] differs from them in computational details. The approach taken was to perform DFT B3LYP/6-31G(d,p)calculations and to supplement them with empirical parameters. Several parametric schemes were explored, one of which was a five-parameter model that consisted of four *atomic* parameters for C, H, N and O (no structure-based parameters) and a single additional parameter for each radical center present. This simple scheme did not provide as good fit as did the more elaborate parametric schemes that included specific structural features, but the fit was acceptable. For a total set of 39 singlet and radical species the simple scheme produced a satisfying MAD (mean absolute deviation) value of 1.51 kcal/mol[7].

The primary objective of the computations described here was to estimate enthalpies of formation and standard entropies for the tetrazine based energetic species. To this end we carried out a series of DFT B3LYP/6-31G(d,p) for the tetrazines and related reference compounds. Since, many of these substances incorporate unique structural features that went beyond our previous TNAZ work, we have also undertaken parallel computations (when molecular size allowed it) with the more sophisticated (and precise) G3(MP2)//B3LYP model.

The calculated heat of formation of 1 is compared with a reported measured value. We also present estimated heats of formation of two novel potential explosives.



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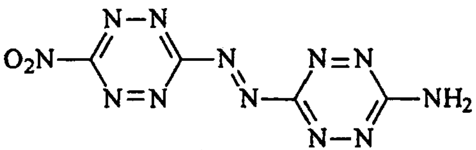

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COMPUTATIONS

The DFT results reported herein were evaluated using the Gaussian G98W suite of programs[8] with complete geometric optimization; the derived frequencies were all positive. The zero-point and thermal corrections used to evaluate enthalpies and entropies at 298.15 K were based on unscaled frequencies. The atomic energies needed to calculate molecular heats of formation are (au per atom): C -38.11689; H -0.58094; N -54.76217; O -75.15317.

In the present B3LYP/6-31G(d,p) calculations no radical species were included. Hence only four of the previously derived[7] correction parameters (kcal/mol) were applied: R(H) +0.676; R(C) -0.603; R(N) +0.492; R(O) -0.597.

The G3(MP2)//B3LYP calculations were performed using the "G3MP2B3" option of the G98W program suite, which employs scaled frequencies for the estimation of the enthalpies and entropies. Corrected enthalpies employed the previously derived[7] correction parameters (kcal/mol): P(H) -0.323; P(C) 0.717; P(N) -0.225; P(O) -0.221.

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RESULTS AND DISCUSSION

Table 1 is a compilation of the calculated heats of formation for those compounds with published experimental heats of formation; Table 2 is a compilation of calculated heats of formation for 10 species for which experimental heats of formation are not available. Table 2 also includes calculated molar entropies, S°, and constant volume heat capacities, C_V, in order to facilitate the calculation of equilibrium constants and the approximate extrapolation of the results to other temperatures.

In Table 1 the enthalpies of formation calculated via the standard B3LYP/6-31G(d,p) and G3(MP2)//B3LYP models as well as the empirically adjusted variations are compared with the experimental values and contrasted with those of the previously cited report of Williams and Whitehead[3]. The mean absolute deviation (MAD) between the calculated and experimental heats of formation for all 14 compounds is 2.82 kcal/mol. In what turns out to be an unanticipated coincidence, the MAD for the empirically adjusted B3LYP/6-31G(d,p) values is also 2.82 kcal/mol. Although inclusion of empirical adjustments appears to make no difference, closer examination reveals a more interesting pattern. First, it should be emphasized that the empirical constants used here were taken *unaltered* from our previous study, which focused on amines and nitro compounds. If the eight azo and hydrazo compounds are excluded, the MAD of the remaining six is only 1.34 kcal/mol, which is in close accord with our previous study and illustrates the merit of the adjustment scheme . The MAD of the separate set of eight azo and hydrazo compounds is 3.94 kcal/mol. This suggests an inherent weakness in the B3LYP/6-31G(d,p) model that might benefit from introduction of a new "azo/hydrazo" parameter. Indeed, if such a parameter were assigned a value of -3.94 kcal/mol (corresponding to a greater than calculated stability), the MAD of the entire set of 14 compounds would be reduced to 1.72 kcal/mol. We did not include this specific correction factor for azo/hydrazo because we felt that the correction parameter would be based on such limited data that it would give a false sense of fit quality.

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The G3(MP2)//B3LYP model is of higher accuracy than the B3LYP/6-31G(d,p) model[9], which comes at the expense of considerably greater computer resources. We have applied the G3(MP2)//B3LYP model (both the original and adjusted versions) to several of the compounds reported here to determine whether the pattern of high $\Delta H_f°$ for the azo and hydrazo compounds persisted. From the results listed in Table 1 it is apparent that original version of the G3(MP2)//B3LYP model is very good (a MAD of 1.67 kcal/mol for the listed 11 compounds) and in keeping with our earlier study, the adjusted version is only slightly better. It is interesting to note that in both the original and adjusted versions the MAD of the hydrazo compounds are positive by 2.72 and 1.72 kcal/mole, respectively. This is an improvement over the original and adjusted B3LYP/6-31G(d,p) models, but still large enough to point to the inherent difficulty of calculating the energies of azo and hydrazo compounds.

Finally, Table 1 includes the results of several calculations using the RHF/6-31G(d,p) model employed by Williams and Whitehead[3] in their extensive compilation of heats of formation of azole, azines and benzazoles. Not surprisingly, the MAD is considerably greater than any of the MAD's for the four B3LYP/6-31G(d,p)./G3(MP2)//B3LYP models reported here.

ISODESMIC EQUILBRIA

The primary objective of this study was to develop protocols to estimate enthalpies of formation for species that incorporate very high levels of nitrogen; the first four entries in Table 2 are representative of the target class. These species are sufficiently large to be beyond our resources for direct

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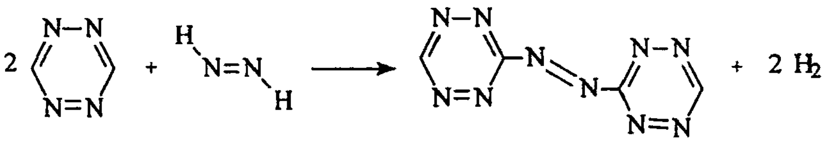
G3(MP2)//B3LYP calculations. We turned to isodesmic equilibria as an alternate means for estimating their corresponding G3(MP2)//B3LYP energies. Another reason for exploring isodesmic equilibria is that they provide insights into the interactions of the structural subunits of the target class, and from these the possibility of designing new high energy species. In order to complete the isodesmic equations the B3LYP//6-31G(d,p) and G3(MP2)//B3LYP values for the five species listed in Table 3 were calculated.

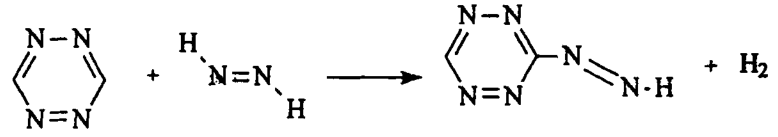
First, consider the heat of formation of the unsubstituted 3,3′-azodi-1,2,4,5-tetrazine, **4**, derived from two tetrazines and one diazine. In this calculation the corrected B3LYP/6-31G(d,p) energies were used. However, the final value result would be the same if uncorrected heats were used because corrections are atom-based and thus cancel. The enthalpy increment for the formation of the intermediate tetrazinyldiazine,5, is compared with the increment for the formation of **4** from 5 plus tetrazine. As required, the sum of the $\Delta\Delta H_f$'s of equations {2} and {3} is equal to that of {1}.


{1}

4

2 (113.24) + 49.59 296.25 2 (-0.64)

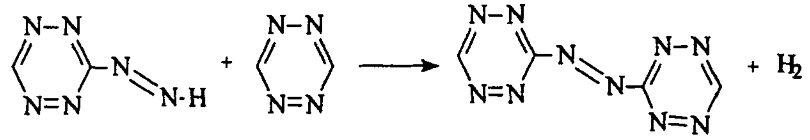
$\Delta\Delta H_f = 18.9$ kcal/mol

 {2}

5

113.24 + 49.59 172.61 -0.64

$\Delta\Delta H_f$ = 9.1 kcal/mol

 {3}

5 4

172.61 + 113.24 296.25 -0.64

$\Delta\Delta H_f$ = 9.8 kcal/mol

Note that the last two values are about equal, which is consistent with the hypothesis that fusion of each tetrazinyl unit with the diazine is approximately additive in enthalpy. If one accepts that the B3LYP/6-31G(d,p) $\Delta\Delta H_f$ of 18.9 kcal/mol derived for equation {1} carries over to that conversion evaluated using G3(MP2)//B3LYP enthalpies, the derived G3(MP2)//B3LYP enthalpy of formation of the unsubstituted 3,3'-azodi-1,2,4,5-terazine, **4**, is 300.4 (corrected) kcal/mol. The corrected B3LYP/6-31G(d,p) heat of formation of **4** is 296.3 kcal/mol. It was shown previously[7] that a simple linear parametric scheme could be used to estimate an individual G3(MP2)//B3LYP heats of formation from the corresponding B3LYP/6-31G(d,p) value.

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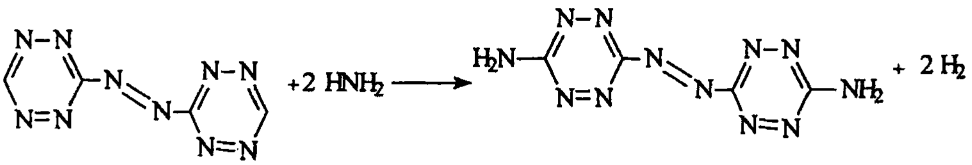
Application of this scheme gives an estimated G3(MP2)//B3LYP heat of formation of **4** of 294.4 kcal/mol, in reasonable agreement with the value of 300.4 kcal/mol derived from the isodesmic approach.

An independent test of the validity of this isodesmic approach is to compare the G3(MP2)//B3LYP heat of formation of the diazine **5** predicted from the B3LYP/6-31G(d,p) enthalpies, with the actual calculated value of 173.17 (corrected) kcal/mol. From equation (2) and the enthalpies for tetrazine, diazine and hydrogen given in Tables 2 and 3, the predicted heat of formation is 173.64 (corrected) kcal/mol, in excellent agreement with the actual value.

Having demonstrated that the isodesmic equilibrium method provides a reasonable route for estimating G3(MP2)//B3LYP enthalpies, we now consider the enthalpy of formation of **1**, the diamino derivative of **4**. From the B3LYP/6-31G(d,p) enthalpies, the $\Delta H_r = \Delta\Delta H_f = -9.9$ kcal/mol.

4 **1**

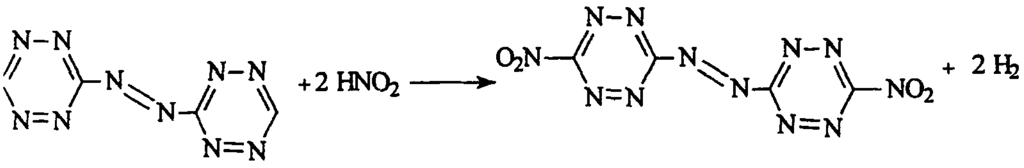


296.25 2 (-6.59) 274.50 2 (-0.64)

$\Delta\Delta H_f = -9.9$ kcal/mol

Combination of this $\Delta\Delta H_f$ with the (estimated) G3(MP2)//B3LYP enthalpy of formation of **4** and the calculated G3(MP2)//B3LYP enthalpies for NH_3 and H_2 gives an estimated G3(MP2)//B3 enthalpy of formation for **1** of 271.3 (corrected) kcal/mol. This is a gas phase enthalpy of formation and can not be compared directly with the measured solid phase heat of formation. The missing heat of sublimation will be considered in the next section.

It is interesting to estimate the G3(MP2)//B3LYP enthalpy of formation of **2** by the same procedure.



4 **2**

296.25 2 (-9.05) 314.26 2 (-0.64)

$\Delta\Delta H_f$ = 34.8 kcal/mol

Combination of this $\Delta\Delta H_f$ with the (estimated) G3(MP2)//B3LYP enthalpy of formation of **4** and the calculated G3(MP2)//B3LYP entalpies for HNO_2 and H_2 gives an estimated G3(MP2)//B3LYP enthalpy of formation of **2** of 317.5 (corrected) kcal/mol.

Now consider the hypothetical disproportionation of two 3's to give 1 and 2. From a local molecular perspective this isodesmic reaction should have a ΔH_r = 0.0. In fact, the B3LYP/6-31G(d,p) ΔH_r is +5.2 kcal/mol. We attribute this non-zero enthalpy to the long range electrostatic interactions of the NH_2 and NO_2 groups, repulsive in the case of 1 and 2 and attractive in 3. This non-zero enthalpy demonstrates a limitation of the isodesmic equilibrium method.

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HEATS OF FORMATION OF SOLIDS

Electronic calculations give heats of formation in the gas phase. For comparison with experimental heats evaluated for the solids, the enthalpy of sublimation must be included. Politzer and co-workers[10] have developed an ingenious scheme based on HF/STO-5G*//HF/STO-3G* wave functions. Following Bader[11], they defined a molecular surface at the 0.001 au contour. The electrostatic potential on this surface was characterized in terms of its average deviation and its positive and negative variances. A balance parameter, a measure of the equality of these variances, was also defined. The heat of sublimation may then be approximated via a three-term linear equation that includes the square of the surface area and the square root of the product of the balance parameter times the sum of the positive and negative variances. A set of 34 experimental heats of sublimation were fitted with a standard deviation of only 2.5 kcal/mol. Rice and co-workers[4] applied the Politzer model to their set of 68 high-energy nitrogen compounds (with readjusted parameters) and achieved a mean absolute deviation of 3.2 kcal/mol.

For the present study we developed a simpler procedure, based on the spirit of the Politzer work. The available molecular mechanics modeling program PCMODEL[12] calculates molecular surface areas(total area and polar area) and volumes, based on atomic radii. In PCMODEL, polar area is the accessible surface area of each N, O and Halogen atom present. It was found that the following linear four-parameter equation fit the same 34 compounds examined by Politzer with a standard deviation of 2.4 kcal/mol.

$$\Delta H_{sub} = A + B * Vol + C \bullet (Polar\ area/Total\ area) + D \bullet \#NO_2's$$

In this equation, the empirically adjusted parameters are (all in kcal/mol): A = -7.2586, B = 0.1331, C = 21.4466, and D = -4.5013. Without inclusion of the D term, the three nitro compounds in the data set deviated markedly (particularly TNT with its three nitro groups). When this model is applied to the Rice data set *without* adjustment of the parameters a mean absolute deviation of 3.0 kcal/mol is found. Although this simple equation appears be as least as predictive as the Politzer model, it must be stressed that it is highly empirical and necessarily misses the electronic detail provided by the Politzer method. The advantage of the present model is that even for large molecules it takes less than a minute to draw a structure in PCMODE1, optimize the geometry and calculate the required volume and area terms.

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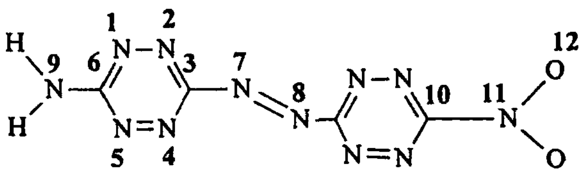
Using this equation the calculated heat of sublimation of **1** is 32.3 kcal/mol. When this combined with the calculated gas phase heat of formation, the estimated solid phase heat of formation is 239.0 kcal/mol with a combined uncertainty of about 5 kcal/mol. The reported solid phase experimental value is 206 kcal/mol][1]. The large discrepancy between the calculated and measured solid state enthalpies of formation merits additional study.

In the same manner the solid state enthalpy of formation of the dinitro analog, **2**, was estimated to be 317.5 - 40.4 = 267.1

kcal/mol; the enthalpy of formation of the amino-nitro derivative, 3, is 291.8 - 36.2 = 255.6 kcal/mol.

INTERATOMIC DISTANCES

To facilitate comparisons of the structures of species considered in the preceding sections, it is helpful to assign atom-numbers in a consistent (arbitrary) sequence, as illustrated below for the amino,nitro bis tetrazine. In Table 4, distances are quoted in Å



units; angles in degrees, computed for the B3LYP/6-31G(d,p) energy-minimized structures. In the corresponding explanatory footnotes, experimental magnitudes obtained from electron diffraction or micro-wave measurements are designated in curly brackets.

CONCLUSIONS

This manuscript summarizes DFT calculations of thermochemical and structural parameters for 14 species, for which enthalpies of formation are cited in the literature. Comparisons between the computed and experimental values provide a measure of the reliance

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one can have in the previously determined four-parameter correction scheme for minimizing deviations between experiment and theory. This scheme was then extended to eleven high-nitrogen based species for which no experimental data are available. Thereby, enthalpies of formation, standard state entropies (ideal gas: simple harmonic oscillators at 298.15K) and converged energy structures were derived.

It is demonstrated that G3(MP2)//B3LYP enthalpies of formation can be reliably estimated from B3LYP/6-31G(d,p) enthalpies by use of corresponding isodesmic equilbria.

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ACKNOWLEDGEMENTS

We thank Dr. Michael A. Hiskey for reviewing this report and for his useful comments.

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TABLE 1: Calculated B3LYP/6-31G(d,p) and G3(MP2)//B3LYP energies and heats of formation with and without empirical corrections (the electronic energies, E_e, are in au; all other energies are in kcal/mol at 298.15 K)

Compound	B3LYP/6-31G(d,p) Calc. E_e	Calc. ΔH_f°	Corr. ΔH_f°	Expt. ΔH_f°	Error no corr.	Error corr.	G3(MP2)//B3LYP Calc. ΔH_f°	Corr. ΔH_f°	Error no corr.	Error corr.	RHF/6-31G(d,p) Calc. ΔH_f°	Error
Benzene	-232.25821	21.79	22.23	19.82[a]	1.97	2.41	18.88	21.24	-0.94	1.42		
Pyridine	-248.29261	33.16	34.02	33.50[a]	-0.34	0.52	32.78	34.53	+0.72	1.03	34.6	1.1
Pyridazine	-264.29362	64.93	66.21	66.50[a]	-1.57	-0.29	66.80	67.93	0.30	1.43	69.0	2.5
Pyrimidine	-264.32948	42.96	44.24	46.80[a]	-3.84	-2.56	44.60	45.73	-2.20	-1.07	43.2	-3.8
Pyrazine	-264.32302	46.86	48.13	46.86[a]	-0.00	1.27	48.86	49.99	0.00	3.13	51.9	5.0
1,3,5-Triazine	-280.36870	51.32	53.02	53.98[a]	-2.66	-0.96	54.30	54.81	0.32	0.83	51.8	-2.2
trans-Azobenzene	-572.77800	101.30	101.81	96.92[b]	4.38	4.89						
cis-Azobenzene	-572.75373	116.05	116.56	109.49[b]	8.35	8.86						
Hydrazine	-111.86866	23.21	26.89	22.79[b]	0.42	4.10	24.67	22.93	1.88	0.14		
3,6-Dihydrazyl tetrazine	-517.70465	123.52	130.31	128.00[c]	-4.48	2.31						
Methylhydrazine	-151.17800	22.48	26.92	22.61[b]	-0.13	4.31	26.68	25.01	4.07	2.40		
1,1-Dimethyl hydrazine	-190.49624	15.69	20.87	20.05[b]	-4.36	0.82	23.11	21.51	3.06	1.56		
1,2-Dimethyl hydrazine	-190.49362	17.62	22.81	21.99[b]	-4.37	0.82	24.39	22.79	2.40	0.80		
Phenylhydrazine	-342.93137	52.90	55.68	48.49[b]	4.41	7.19	50.94	52.20	2.45	3.71		
		MAD (no azo or hydrazo)			1.73	1.34	MAD (all)		1.67	1.39		
		MAD (all)			2.82	2.82						

(a) ref 13. (b) J.B. Pedley, R.D. Naylor, and S.P. Kirby, Thermochemical Data of Organic Compounds. 2nd Ed. Chapman and Hall, New York, 1986. (c) D. Chavez, M.A. Hiskey, and C. Joh, J. Energetic Materials 17, 357 (1999)

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TABLE 2: Calculated B3LYP/6-31G(d,p)energies and heats of formation in kcal/mol at 298.15 K (with and without empirical corrections) and other thermochemical parameters plus selected G3(MP2)//B3LYP heats of formation ()

Compound	Calc. E_e	Calc. ΔH_f	Corr. ΔH_f	S° eu	C_v cal/mol•K	G3(MP2)//B3LYP ΔH_f Calc.	G3(MP2)//B3LYP ΔH_f Corr.
6,6′-Diamino-3,3′-Azodi-1,2,4,5-tetrazine, 1	-811.64933	268.30	274.50	116.9	49.02		
6,6′-Dinitro-3,3′-Azodi-1,2,4,5-tetrazine, 2	-1109.83881	313.18	314.26	135.1	54.82		
6-Amino-6′-nitro-3,3′-Azodi-1,2,4,5-tetrazine,3	-960.74830	288.15	291.79	127.0	51.77		
3,3′-Azodi-1,2,4,5-tetrazine, 4	-700.88810	292.39	296.25	103.7	37.09		
1,2,4,5-Tetrazine	-296.32385	111.13	113.24	68.7	14.20	115.85	115.74
3-Amino-1,2,4,5-tetrazine	-351.70193	100.61	103.89	76.0	20.25		
3-Nitro-1,2,4,5-tetrazine	-500.80186	119.89	120.62	84.1	23.00		
1,2,4,5-Tetrazinyldiazine, 5	-405.76626	169.52	172.61	79.5	21.15	173.73	173.17
3,6-Diamino-1,2,4,5-tetrazine	-407.07156	95.44	99.89	80.9	25.80		
3,6-Dinitro-1,2,4,5-tetrazine	-705.27508	131.63	130.96	99.8	31.89		
1,4-Diaminobenzene	-342.97078	27.90	30.68	82.8	29.16		
1,4-Dinitrobenzene	-641.25242	16.16	13.81	96.4	34.28		

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TABLE 3: Calculated B3LYP/6-31G(d,p) and G3(MP2)//B3LYP energies and heats of formation in kcal/mol at 298.15 K (with and without empirical corrections) and other thermochemical parameters for use in calculating isodesmic reaction enthalpies.

Compound	Calc. E_e	Calc. ΔH_f	Corr. ΔH_f	S^o eu	C_v cal/mol•K	G3(MP2)//B3LYP ΔH_f Calc.	G3(MP2)//B3LYP ΔH_f Corr.
H-H	-1.17854	-1.99	-0.64	31.1	4.97	-1.08	-1.72
$H-NH_2$	-56.55777	-9.11	-6.59	46.0	6.33	-10.13	-11.33
$H-NO_2$	-205.68968	-9.01	-9.05	56.9	7.17	-9.62	-10.61
(E)-HN=NH	-110.64301	47.25	49.59	52.1	6.30	48.17	47.08
(Z)-HN=NH	-110.63386	52.55	54.88	52.2	6.34	53.40	52.31

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TABLE 4: Summary of Computed Interatomic Distances

	C_6N_1	N_1N_2	N_2C_3	C_3N_7	C_6N_9	N_7N_8	$C_{10}N_{11}$	$N_{11}O_{12}$	ref
	tet = 1,2,4,5 tetrazine; (tr) = trans								
1,2,4,5-tetrazine	1.340	1.325	1.340						a
3-aminotetrazine	1.340	1.316	1.357		1.350				b
3,6-diaminotetrazine	1.349	1.316	1.349	1.369	1.369				c
3,6-dihyrazinyltetrazine (tr)	1.351	1.315	1.350	1.370	1.370	1.406			d
3-nitrotetrazine	1.341	1.325	1.329				1.489	1.224	e
3,6-dinitrotetrazine	1.330	1.323	1.330		1.487		1.487	1.221	f
3-azoetrazine (5)	1.340	1.322	1.341	1.429			1.247		g
3,3'-azobis tetrazine (tr)(4)	1.341	1.322	1.341	1.429			1.247		h
3,3'-azobis(6-amino tet)(tr)(1)	1.358	1.310	1.347	1.412	1.346	1.258			j
3-amino-3'nitro azobis tet (tr)(3)	1.364	1.306	1.347	1.410	1.339	1.257	1.486	1.227	k
3,3'-azobis(6-nitro tet)(tr)(2)	1.330	1.319	1.344	1.422	1.486	1.251	1.486	1.222	m

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FOOTNOTES to TABLE 4

a. The tetrazine ring is somewhat compressed. The internal angles at C are 126.5; at N : 116.7. The C—H bond length is 1.086.

b. Conjugation with the amino group is indicated by additional compression of the tetrazine ring and extension of the attached N_2-C3 bond length. The internal bond angles at the C's are decreased slightly, to 125.5. More striking is the significantly short C—NH_2 bond length, compared to that in H_3C—NH_2 : 1.464 (1.471). In trimethylamine the corresponding distance is (1.454); in aniline (1.402).

c. Para-substitution additionally stretches the C—N bonds in the ring; the internal angles at C's are 124.6. The external C—NH_2 is longer than in 3-aminotetrazine. In para-diamino-benzene the computed C—NH_2 is 1.409 (1.424), which is about 0.05 A longer than in the analogous tetrazine.

d. Bond lengths in dihyrazinyltetrazine are close to those in the diamino species. The calculated N—N separation in hydrazine is 1.437 (1.449), but in 1,2 dimethyl hydrazine the reported value is (1.419). In phenyl hydrazine N—N is 1.411; C—N is 1.404, both being longer than in the analogous tetrazine.

e. In the tetrazine ring, the N_2-C_3 bond length is reduced by NO_2 substitution, in contrast to extension in 3-amino tetrazine. The internal bond angles at C is 128.6. The C—NO_2 separation is shorter than in nitromethane, 1.499 (1.488), but longer than in nitrobenzene (1.478).

f. The internal bond angles at the nitrogens are lower --- 115.7. In para-dinitro benzene C—NO_2 = 1.479 (1.463).

g. In the singly substituted azo-tetrazine and in 3,3' azo-bis tetrazine corresponding bonds have equal lengths.

h. The C_3—N_7 bond length is midway between that in the di-amino and di-nitrotetrazines. In trans azo-benzene the corresponding C—N is 1.419, while N==N is 1.261. In trans azo methane C—N is (1.474) ; N==N is (1.254).

j. Substitution of the -NH_2 moieties at the terminae of azo-bis tetrazine leads to changes in bond lengths of 0.01 to 0.02 A. However, bond angles remain unaltered to within 1°.

k. Contrary to expectations, corresponding bond lengths in this mixed species are not intermediate between azo-bis (6-diamino ...) and azo-bis (6-dinitro...). However, the bond angles are essentially identical with those in azo-bis(6-diamino...).

m. $\angle N_1C_6N_5$ = 115.8° (which is 2° smaller) and $\angle N_2C_3N_4$ = $\angle N_1C_6N_5$ = 128.3° (which are about 3° larger) than in the corresponding amino species.