

1350  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  7.2 (m, 14 H), 4.9 (m, 2 H);  $^{19}\text{F}$  NMR  $\delta$  -121.5 (s). Anal. Calcd for  $\text{C}_{22}\text{H}_{16}\text{F}_2\text{N}_2\text{O}_4$ : C, 64.39; H, 3.93; F, 9.26; N, 6.82. Found: C, 64.14; H, 4.09; F, 9.18; N, 6.96.

**endo-5,exo-6-Difluoro-5,6-dinitrobicyclo[2.2.1]hept-2-ene.** A solution of 1,2-dicyclodinitroethylene (0.299 g, 1.94 mmol) and freshly distilled cyclopentadiene (1.5 g, 23 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was stirred under nitrogen for 10 min at ambient temperature. The solvent was evaporated and the residual oil was chromatographed (silica gel,  $\text{CH}_2\text{Cl}_2$ ) to give 0.209 g (49%) of *endo-5,exo-6-difluoro-5,6-dinitrobicyclo[2.2.1]hept-2-ene*, mp 81–82 °C: IR 1560, 1320  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  6.6 (m, 1 H), 6.3 (m, 1 H), 3.5 (m, 2 H), 2.6 (m, 1 H), 2.3 (m, 1 H);  $^{19}\text{F}$  NMR  $\delta$  -121.03 (bs). Anal. Calcd for  $\text{C}_7\text{H}_6\text{F}_2\text{N}_2\text{O}_4$ : C, 38.19; H, 2.75; F, 17.26. Found: C, 38.20; H, 2.89; F, 16.98.

**X-ray analysis of *trans*-1,2-difluorodinitroethylene:**  $\text{C}_2\text{F}_2\text{N}_2\text{O}_4$ ,  $M_r = 154.0$ , orthorhombic space group *Pbca*,  $a = 9.375$  (2),  $b = 0.122$  (3), and  $c = 10.505$  (3) Å,  $V = 996.8$  (4) Å<sup>3</sup>,  $Z = 8$ ,  $D_X = 2.053$  Mg  $\text{m}^{-3}$ ,  $\lambda(\text{Mo K}\alpha) = 0.71073$  Å,  $\mu = 0.22$  mm<sup>-1</sup>,  $F(000) = 608$ , data collection  $T = 201$  K, final  $R = 0.055$ ,  $wR = 0.066$  for 578 independent reflections with  $F_o > 3\sigma(F_o)$ .

A clear colorless 0.01 × 0.42 × 0.51 mm crystal grown by sublimation was used for data collection on an automated Nicolet R3m/V diffractometer with incident beam monochromator, and 20 centered reflections within  $22 < 2\theta < 39^\circ$  were used for determining lattice parameters.  $(\sin \theta)/\lambda_{\text{max}} = 0.54$  Å<sup>-1</sup>; range of  $hkl$ ,  $-10 \leq h \leq 10$ ,  $0 \leq k \leq 10$ , and  $0 \leq l \leq 11$ . Standard reflections 400, 040, 004 monitored every 100 reflections with random variations up to  $\pm 2.5\%$  over data collection,  $\theta/2\theta$  mode, scan width  $[2\theta(K_{\alpha 1}) - 0.9]$  to  $[2\theta(K_{\alpha 2}) + 0.9]^\circ$ ,  $2\theta$  scan rate 60.0° min<sup>-1</sup> (rapid due to volatile crystal); 1534 reflections measured, 654 unique, 587 observed with  $F_o > 3\sigma(F_o)$ ;  $R_{\text{int}} = 0.042$ . Data was corrected for Lorentz and polarization, but not absorption effects. Structure was solved by direct methods. The least-squares refinement minimized the quantity  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1/[\sigma^2(|F_o|) + g \cdot (F_o)^2]$ ,  $g = 0.00023$ . Secondary extinction parameter  $p = 0.0029$  (8) in  $F_c^{\text{obs}} = F_c/[1.0 + 0.002(p)F_o^2/\sin(2\theta)]^{0.25}$ . There were 92 parameters refined: all atom coordinates, anisotropic temperature parameters for nonhydrogen atoms; the hydrogen atoms were assigned fixed isotropic thermal parameters.  $(\Delta/\sigma)_{\text{max}} = 0.01$ ,  $R = 0.055$ ,  $wR = 0.066$ ,  $S = 2.88$ . Final difference Fourier excursions 0.51 and  $-0.28$  e Å<sup>-3</sup>. Atomic scattering factors from *International Tables for Crystallography*.<sup>6</sup> The programs used for structure solution, refining, and plotting are part of SHELXTL.<sup>7,8</sup>

(6) *International Tables for X-ray Crystallography*, Vol. IV; Kynoch Press: Birmingham, England, 1974 (present distributor D. Reidel, Dordrecht).

**X-ray analysis of *endo-5,exo-6-difluoro-5,6-dinitrobicyclo[2.2.1]hept-2-ene*:**  $\text{C}_7\text{H}_6\text{F}_2\text{N}_2\text{O}_4$ ,  $M_r = 220.14$ , orthorhombic space group *P22<sub>1</sub>2<sub>1</sub>*,  $a = 6.033$  (3),  $b = 11.629$  (4), and  $c = 12.501$  (4) Å,  $V = 877.1$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $D_X = 1.667$  Mg  $\text{m}^{-3}$ ,  $\lambda(\text{Cu K}\alpha) = 1.54183$  Å,  $\mu = 1.42$  mm<sup>-1</sup>,  $F(000) = 448$ , data collection  $T = 295$  K, final  $R = 0.045$ ,  $wR = 0.047$  for 736 independent reflections with  $F_o > 3\sigma(F_o)$ .

A clear colorless 0.05 × 0.40 × 0.25 mm crystal recrystallized from carbon tetrachloride was used for data collection on an automated Nicolet R3m/V diffractometer with incident beam monochromator; 25 centered reflections within  $45 < 2\theta < 88^\circ$  were used for determining lattice parameters.  $(\sin \theta)/\lambda_{\text{max}} = 0.56$  Å<sup>-1</sup>; range of  $hkl$ ,  $0 \leq h \leq 6$ ,  $0 \leq k \leq 13$ , and  $0 \leq l \leq 14$ . Standard reflections 400, 040, 006 monitored every 100 reflections showed a linear decay of  $\pm 15\%$  over data collection,  $\theta/2\theta$  mode, scan width  $[2\theta(K_{\alpha 1}) - 1.0]$  to  $[2\theta(K_{\alpha 2}) + 1.0]^\circ$ ,  $2\theta$  scan rate 60° min<sup>-1</sup> (rapid due to volatile crystal, full data set collected in 4 h); 855 reflections measured, 841 unique, 736 observed with  $F_o > 3\sigma(F_o)$ ;  $R_{\text{int}} = 0.030$ . Data was corrected for Lorentz and polarization, and an empirical absorption correction was applied. The maximum and minimum transmission values were 0.77 and 0.72. Structure was solved by direct methods. The least-squares refinement minimized the quantity  $\sum w(|F_o| - |F_c|)^2$ , where  $w = 1/[\sigma^2(|F_o|) + g \cdot (F_o)^2]$ ,  $g = 0.00023$ . Secondary extinction parameter  $p = 0.012$  (1) in  $F_c^{\text{obs}} = F_c/[1.0 + 0.002(p)F_o^2/\sin(2\theta)]^{0.25}$ . There were 137 parameters refined: atom coordinates and anisotropic temperature parameters for non-hydrogen atoms; the hydrogen atoms riding on covalently bonded carbon atoms (C-H distance set at 0.96 Å and angles involving H atoms idealized at tetrahedral or trigonal values, as appropriate).  $(\Delta/\sigma)_{\text{max}} = 0.04$ ,  $R = 0.045$ ,  $wR = 0.047$ ,  $S = 1.41$ . Final difference Fourier excursions 0.16 and  $-0.18$  e Å<sup>-3</sup>. Atomic scattering factors from *International Tables for Crystallography*.<sup>6</sup> The programs used for structure solution, refining, and plotting are part of SHELXTL.<sup>7,8</sup>

**Acknowledgment.** This work was supported by the U.S. Army Research Office and the Office of Naval Research, Mechanics Division. We thank Dr. M. Coburn of Los Alamos National Laboratory for the <sup>14</sup>N NMR spectrum.

(7) Sheldrick, G. M. "SHELXTL80, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data", University of Göttingen, Federal Republic of Germany, 1980.

(8) Tables of atom coordinates, bond distances and angles, structure factors, anisotropic thermal parameters, and hydrogen coordinates are included in the supplementary material.

## The Unknown Unsubstituted Tetrazines: 1,2,3,4-Tetrazine and 1,2,3,5-Tetrazine

J. Russell Thomas,\* Geoffrey E. Quelch, and Henry F. Schaefer III

Center for Computational Quantum Chemistry,<sup>†</sup> University of Georgia, Athens, Georgia 30602

Received June 1, 1990

Ab initio theoretical methods have been used to determine the equilibrium geometry of the unsubstituted 1,2,3,4- and 1,2,3,5-tetrazines. Double zeta (DZ) and double zeta plus polarization (DZP) basis sets have been used at both the self-consistent field (SCF) and single and double excitation configuration interaction (CISD) levels of theory. Harmonic vibrational frequencies and infrared intensities have been evaluated at the SCF level of theory. Comparisons between these and previous results at the SCF level using smaller basis sets have been made. The 1,2,3,5-tetrazine is predicted to lie 8 kcal mol<sup>-1</sup> below the experimentally characterized s-tetrazine (i.e., 1,2,4,5-tetrazine). The work strongly suggests renewed experimental efforts toward the laboratory identification of 1,2,3,5-tetrazine.

### Introduction

Of the three possible tetrazine molecules (a tetrazine is a benzene molecule with four CH units replaced by ni-

trogen atoms), only the 1,2,4,5-tetrazine (also called s-tetrazine) has been unambiguously characterized experimentally.<sup>1-3</sup> The other two isomers, 1,2,3,4- and 1,2,3,5-

\* CCQC Summer Research Fellow, 1989.

<sup>†</sup> CCQC contribution no. 104.

(1) Curtius, T.; Darapsky, A.; Muller, F. *Chem. Ber.* 1907, 40, 84.  
(2) Koenigsberger, J.; Vogt, K. *Phys. Z.* 1913, 14, 1269.

Table I. Theoretical Results for 1,2,3,4-Tetrazine<sup>a</sup>

	PPP, ref 18	SPO, ref 18	ab initio				
			SCF/6-31G, <sup>b</sup> ref 23	SCF/DZ <sup>c,d</sup>	CISD/DZ <sup>d</sup>	SCF/DZP <sup>d</sup>	CISD/DZP <sup>d</sup>
$r_1$			1.067	1.067 [1.064]	1.081	1.076 [1.074]	1.080 [1.079]
$r_2$	1.298	1.290	1.318	1.325 [1.339]	1.342	1.302 [1.322]	1.314 [1.331]
$r_3$	1.336	1.352	1.329	1.338 [1.319]	1.383	1.314 [1.292]	1.330 [1.310]
$r_4$	1.447	1.465	1.390	1.399	1.420	1.395	1.396
$r_5$	1.272	1.262	1.298	1.310 [1.319]	1.335	1.276 [1.292]	1.297 [1.310]
$\theta_1$			119.4	123.4	123.0	123.1	123.0
$\theta_2$			119.3	119.4	120.3	119.3	119.8
$\theta_3$			119.4	119.3	118.4	118.7	118.3
$\theta_4$			121.3	121.3	121.3	122.0	121.9
$E/H$			-294.38425 <sup>e</sup>	-294.43265		-294.62168	
$E_{\text{CISD}}/H$					-294.94515		-295.35791
$E_{\text{CISD+q}}/H$					-295.03008		-295.48374

<sup>a</sup> Geometrical parameters (Å and deg) are defined in Figure 1. All energies are at the appropriate optimized geometries unless otherwise stated. The values in brackets are analogous values for *s*-tetrazine. <sup>b</sup> At the SCF/3-21G level (optimized geometry), the energy was -292.85977, and at 3-21G+//3-21G, the energy was -292.89846, from ref 24. <sup>c</sup> Energy of -293.51233 by a SCF/DZ study in refs 19 and 20; geometries were taken from other azines. <sup>d</sup> This work. <sup>e</sup> Energy of -294.56479 with a 6-31G\* basis at the 6-31G geometry.

tetrazine, have been the subject of synthetic studies, but few unequivocal products have been demonstrated.

The first claimed synthesis of the 1,2,3,5-tetrazine was reported in 1979 by Ege and Gilbert.<sup>4</sup> The species synthesized was a large structure containing the tetrazine ring; however, the carbon on position 4 bore a carbonyl oxygen and also a second ring was fused at the 5,6-positions; therefore, this structure is unlikely to be an aromatic system. Further attempts to synthesize the 1,2,3,5-tetrazine were reported by Baydar, Boyd, Lindley, and Walton.<sup>5</sup> They too were unsuccessful at producing an unsubstituted 1,2,3,5-tetrazine since their product was substituted at the 3-position and also contained a carbonyl oxygen at the 4-position. The authors claim that the 1,2,3,4-tetrazines are unknown, with 1,2,3,5-tetrazines occurring in complex cyano-amino derivatives.<sup>6</sup>

In more recent work by Butler, Cunningham, McArdle, and O'Halloran,<sup>7</sup> a claim was made that "...the 1,2,3,5 [tetrazine] species are by far the rarest and least studied class. Few derivatives are known and most involve condensed forms of the ring." The new 1,2,3,5-tetrazine derivative reported in this work was a 2,5-substituted species. The central tetrazine ring displays X-ray-determined bond lengths of  $r(\text{N}_1\text{N}_2) = 1.39 \text{ \AA}$ ,  $r(\text{N}_3\text{N}_4) = 1.28 \text{ \AA}$ , and  $r(\text{C}_4\text{N}_5) = 1.43 \text{ \AA}$  as compared to values for individual alternating single and double bond values of  $r(\text{N}-\text{N}) = 1.41 \text{ \AA}$ ,  $r(\text{N}=\text{N}) = 1.25 \text{ \AA}$ ,  $r(\text{C}-\text{N}) = 1.45 \text{ \AA}$  and  $r(\text{C}=\text{N}) = 1.27 \text{ \AA}$ . This demonstrates that the tetrazine ring in this molecule is not aromatic; indeed the ring takes up a boat conformation.

The synthesis of a structure containing a 1,2,3,4-tetrazine ring was reported in 1982 by Cheng.<sup>8</sup> The species generated was not isolable, but the conjectured structure would be a true tetrazine due to ring fusion at the 5,6-positions (carbon) only. Another synthesis of a 1,2,3,4-tetrazine derivative was reported<sup>9</sup> in 1982. In this work the tetrazine ring was ring-fused at the 2,3-positions and

also substituted at the 1,4-positions; therefore this tetrazine is again unlikely to be aromatic. Another claim to the production of the first 1,2,3,4-tetrazine has been published recently.<sup>10</sup> The ring produced in this work was fused at the 5,6-positions to a triazole ring. Bond alternation is also evident, i.e.,  $r(\text{N}_1\text{N}_2) = 1.325 \text{ \AA}$ ,  $r(\text{N}_2\text{N}_3) = 1.405 \text{ \AA}$ ,  $r(\text{N}_3\text{N}_4) = 1.308 \text{ \AA}$ ,  $r(\text{N}_4\text{C}_5) = 1.348 \text{ \AA}$ ,  $r(\text{C}_5\text{C}_6) = 1.444 \text{ \AA}$ , and  $r(\text{C}_6\text{N}_1) = 1.268 \text{ \AA}$ . Strictly speaking,  $r(\text{N}_1\text{N}_2)$  should equal  $r(\text{N}_3\text{N}_4)$ ; similarly  $r(\text{C}_6\text{N}_1)$  should equal  $r(\text{C}_5\text{N}_4)$ . However, the ring is planar, as would be expected for an aromatic system, and this evidence allows the authors to claim that the tetrazine ring is aromatic.

A number of low-level theoretical studies have been published on the unsubstituted tetrazines using a variety of methods. Detailed comparisons between the theoretical results will be made in the discussion section. The experimentally well-characterized *s*-tetrazine molecule has been the subject of a number of theoretical studies by this group<sup>11</sup> and so will not be discussed in any detail except with reference to the 1,2,3,4- and 1,2,3,5-tetrazine results.

### Theoretical Methods

Two Gaussian-type orbital basis sets have been utilized in this work. The first was the standard Huzinaga-Dunning double zeta (DZ) basis<sup>12</sup> designated C,N (9s5p/4s2p) with H (4s/2s) giving a total of 64 contracted functions. A larger basis was constructed by the addition of a set of polarization functions at all centers to the DZ basis, denoted DZP and containing 106 contracted Gaussian functions. For the carbon and nitrogen atoms the polarization functions used had exponents of  $\alpha_d = 0.75$  and 0.80, respectively, with a p-type exponent for hydrogen of  $\alpha_p = 0.75$ . Cartesian Gaussian-type functions were used throughout. For all theoretical treatments the hydrogen *s* functions were scaled by a factor of 1.2.

Molecular geometries at the SCF level were obtained by using analytic gradients of the energy.<sup>13</sup> Harmonic vibrational frequencies and infrared intensities at the minimum energy structure were evaluated by analytic second derivatives of the energy,<sup>14</sup> with

(3) Wiley, P. F. *1,2,3,4-Tetrazines*; Weissberger, A., Taylor, E. C., Eds.; Wiley: New York, 1978; p 1073.

(4) Ege, G.; Gilbert, K. *Tetrahedron Lett.* 1979, 44, 4253.

(5) Baydar, A. E.; Boyd, G. V.; Lindley, P. F.; Walton, A. R. *J. Chem. Soc., Perkin Trans. 1* 1985, 415.

(6) Kubo, K.; Nonaka, T.; Odo, K. *Bull. Chem. Soc. Jpn.* 1976, 49, 1339.

(7) Butler, R. N.; Cunningham, D.; McArdle, P.; O'Halloran, G. A. *J. Chem. Soc., Chem. Commun.* 1988, 232.

(8) Chang, S.-J. *Synth. Commun.* 1982, 12, 673.

(9) Sayed, G. H.; Abd Elhalim, M. S.; El-Kady, M. Y.; Abd Elwahab, L. M. *Indian J. Chem.* 1982, 21B, 589.

(10) Kaihoh, T.; Itoh, T.; Yamaguchi, K.; Ohsawa, A. *J. Chem. Soc., Chem. Commun.* 1988, 1608.

(11) (a) Scheiner, A. C.; Scuseria, G. E.; Schaefer, H. F. *J. Am. Chem. Soc.* 1986, 108, 8160. (b) Scheiner, A. C.; Schaefer, H. F. *J. Chem. Phys.* 1987, 87, 3539. (c) Scuseria, G. E.; Scheiner, A. C.; Lee, T. J.; Rice, J. E.; Schaefer, H. F. *J. Chem. Phys.* 1987, 86, 2881. (d) Scuseria, G. E.; Schaefer, H. F. *J. Phys. Chem.* 1990, 94, 5552.

(12) (a) Huzinaga, S. *J. Chem. Phys.* 1965, 42, 1293. (b) Dunning, T. H., Jr. *J. Chem. Phys.* 1970, 53, 2823.

(13) (a) Pulay, P. *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum: New York, 1977; Vol. 4, pp 153-185. (b) Goddard, J. D.; Handy, N. C.; Schaefer, H. F. *J. Chem. Phys.* 1979, 71, 1525.

Table II. Theoretical Results for 1,2,3,5-Tetrazine<sup>a</sup>

	PPP, ref 18	SPO, ref 18	ab initio				
			SCF/6-31G, <sup>b</sup> ref 23	SCF/DZ <sup>c,d</sup>	CISD/DZ <sup>d</sup>	SCF/DZP <sup>d</sup>	CISD/DZP <sup>d</sup>
$r_1$			1.065	1.066 [1.064]	1.079	1.076 [1.074]	1.081 [1.079]
$r_2$	1.334	1.339	1.327	1.331 [1.339]	1.352	1.314 [1.322]	1.323 [1.331]
$r_3$	1.339	1.346	1.334	1.342 [1.339]	1.363	1.325 [1.322]	1.333 [1.331]
$r_4$	1.299	1.300	1.313	1.322 [1.319]	1.356	1.293 [1.292]	1.311 [1.310]
$\theta_1$			119.3	119.5	119.1	118.7	118.5
$\theta_2$			123.4	123.4	124.1	124.9	125.3
$\theta_3$			119.1	119.0	118.7	118.2	118.2
$\theta_4$			120.2	120.1	119.7	121.0	120.5
$E/H$			-294.42156 <sup>e</sup>	-294.46766		-294.66213	
$E_{\text{CISD}}/H$					-294.97596		-295.39533
$E_{\text{CISD+Q}}/H$					-295.05863		-295.51904

<sup>a</sup> Geometrical parameters (Å and deg) are defined in Figure 1. All energies are at the appropriate optimized geometries unless otherwise stated. The values in brackets are analogous values for *s*-tetrazine. <sup>b</sup> At the SCF/3-21G level (optimized geometry), the energy was -292.90266, and at 3-21G+//3-21G, the energy was -292.94217, from ref 24. <sup>c</sup> Energy of -293.54386 by a SCF/DZ study in ref 19 and 20; geometries were taken from other azines. <sup>d</sup> This work. <sup>e</sup> Energy of -294.60474 with a 6-31G\* basis at the 6-31G geometry.

Table III. Relative Energies ( $\Delta E$ ), Total Energies ( $E$ ), Heats of Formation ( $\Delta H_f$ ), and Heats of Dissociation to Most Stable Products ( $\Delta H_d$ ) for the Tetrazines<sup>a</sup>

ref	method	value	1,2,3,4	1,2,4,5	1,2,3,5
18	PPP	$\Delta H_f/eV$	34.264 ± 0.035	34.600 ± 0.041	35.026 ± 0.060
		$\Delta\Delta H_f$	17.6	9.8	0.0
19	SCF/DZ	$E/H$	-293.51233	-293.47477	-293.54386
20		$\Delta E$	19.8	43.4	0.0
21	MNDDO/1	$\Delta H_f$	130.5	125.6	137.1
		$\Delta\Delta H_f$	6.6	11.5	0.0
		$\Delta H_d$	-76.2	-63.2	-74.7
22	MNDO	$\Delta H_f$	71.3	68.9	63.9
	/4-31G	$\Delta\Delta H_f$	7.4	5.0	0.0
23	SCF/STO-3G	$\Delta E$	13.8	5.1	0.0
	3-21G	$\Delta E$	26.9	8.3	0.0
	6-31G	$\Delta E$	23.4	6.6	0.0
	6-31G*//6-31G	$\Delta E$	25.1	8.9	0.0
24	MNDO	$\Delta E$	7.4	4.9	0.0
	AM1	$\Delta E$	12.4	-0.6	0.0
	SCF/3-21G	$\Delta E$	26.9	8.3	0.0
	3-21G+//3-21G	$\Delta E$	27.4	9.4	0.0
this work <sup>b</sup>	SCF/DZ	$\Delta E$	22.0	6.8	0.0
	SCF/DZP	$\Delta E$	25.4	9.2	0.0
	CISD(+Q)/DZ	$\Delta E$	19.3 (17.9)	-	0.0
	CISD(+Q)/DZP	$\Delta E$	23.5 (22.2)	8.5 (8.0)	0.0

<sup>a</sup> All energies are in kcal mol<sup>-1</sup> unless stated otherwise. <sup>b</sup> Values for 1,2,4,5-tetrazine are taken from ref 11.

infrared intensities evaluated within the double harmonic approximation.<sup>15</sup> The effects of electron correlation were investigated within the configuration interaction, single and double excitation (CISD) model with CISD geometries optimized by utilizing analytic gradients<sup>16</sup> of the CISD energy. All molecular orbitals were included in the CI expansion except the carbon and nitrogen 1s orbitals. CISD energy values (denoted +Q subsequently) have been corrected for the unlinked quadruple excitations using the method of Davidson.<sup>17</sup>

(14) (a) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* 1979, S13, 225. (b) Saxe, P.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* 1982, 72, 131. (c) Osamura, Y.; Yamaguchi, Y.; Saxe, P.; Vincent, M. A.; Gaw, J. F.; Schaefer, H. F. *J. Chem. Phys.* 1982, 72, 131.

(15) Yamaguchi, Y.; Frisch, M.; Gaw, J.; Schaefer, H. F.; Binkley, J. S. *J. Chem. Phys.* 1986, 84, 2262.

(16) (a) Brooks, B. R.; Laidig, W. D.; Saxe, P.; Goddard, J. D.; Yamaguchi, Y.; Schaefer, H. F. *J. Chem. Phys.* 1980, 72, 4652. (b) Rice, J. E.; Amos, R. D.; Handy, N. C.; Lee, T. J.; Schaefer, H. F. *J. Chem. Phys.* 1986, 85, 963.

(17) Davidson, E. R. *The World of Quantum Chemistry*; Daudel, R., Pullman, B., Eds.; Reidel: Dordrecht, Holland, 1974; pp 17-30.

(18) Dewar, M. J. S.; Gleicher, G. J. *J. Chem. Phys.* 1966, 44, 759.

(19) Palmer, M. H.; Gaskell, A. J.; Findlay, R. H. *Tetrahedron Lett.* 1973, 47, 4659.

(20) Palmer, M. H.; Gaskell, A. J.; Findlay, R. H. *J. Chem. Soc., Perkin Trans. 2* 1974, 778.

(21) Dewar, M. J. S. *Pure Appl. Chem.* 1975, 44, 767.

(22) Fos, E.; Vilarrasa, J.; Fernández, J. *J. Org. Chem.* 1985, 50, 4894.

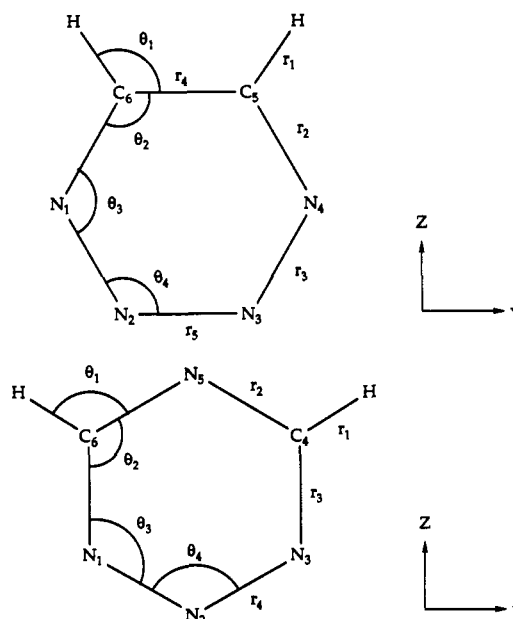
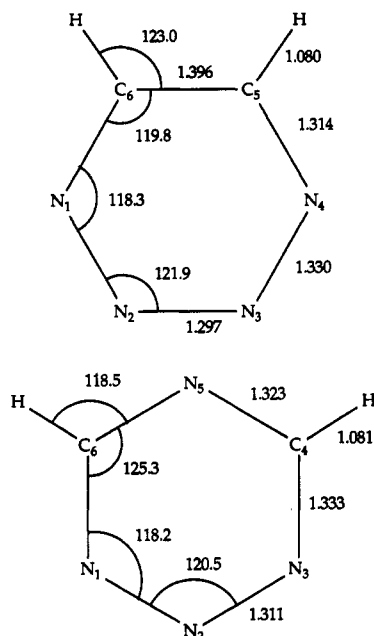


Figure 1. Geometrical structures, axis system, and unique internal coordinate definitions for 1,2,3,4-tetrazine and 1,2,3,5-tetrazine.



**Figure 2.** Geometrical structures for 1,2,3,4-tetrazine and 1,2,3,5-tetrazine at the CISD/DZP level, the highest level of theory considered in this research.

**Table IV.** Theoretical Predicted Harmonic Vibrational Frequencies (in  $\text{cm}^{-1}$ ) and Infrared Intensities (in  $\text{km mol}^{-1}$ ) for 1,2,3,4-Tetrazine at the DZP/SCF Level

$\omega$ , $\text{cm}^{-1}$	$I$ , $\text{km mol}^{-1}$	symmetry	assignment (major components) <sup>a</sup>
1	3401	A <sub>1</sub>	$\nu_s(\text{CH})$
2	3385	B <sub>2</sub>	$\nu_s(\text{CH})$
3	1787	A <sub>1</sub>	$\nu(\text{CC}), \nu_s(\text{CN}), \delta_s(\text{HCN}), \nu(\text{N}_2\text{N}_3)$
4	1773	B <sub>2</sub>	$\nu_s(\text{CN})$
5	1543	B <sub>2</sub>	$\delta_s(\text{HCN}), \nu_s(\text{N}_1\text{N}_2)$
6	1504	A <sub>1</sub>	$\delta_s(\text{HCN}), \nu(\text{N}_2\text{N}_3)$
7	1274	B <sub>2</sub>	$\nu_s(\text{N}_1\text{N}_2), \delta_s(\text{HCN}), \nu_s(\text{CN})$
8	1229	A <sub>1</sub>	$\delta_s(\text{HCN}), \nu(\text{N}_2\text{N}_3), \nu(\text{CC})$
9	1184	A <sub>1</sub>	$\nu_s(\text{CN}), \nu(\text{N}_2\text{N}_3), \nu(\text{CC})$
10	1180	B <sub>2</sub>	$\delta_s(\text{NHN}), \delta_s(\text{CCN})$
11	1107	A <sub>2</sub>	oop H
12	965	B <sub>1</sub>	oop H
13	898	A <sub>1</sub>	$\nu_s(\text{N}_1\text{N}_2), \nu(\text{CC}), \nu(\text{N}_2\text{N}_3)$
14	895	A <sub>2</sub>	$\tau(\text{NHN})$
15	784	B <sub>2</sub>	$\delta_s(\text{CCN})$
16	710	A <sub>1</sub>	$\delta_s(\text{CCN})$
17	416	B <sub>1</sub>	$\tau(\text{CNHN})$
18	387	A <sub>2</sub>	$\tau(\text{CNHN})$

<sup>a</sup> Abbreviations:  $\nu$ , stretch;  $\delta$ , deformation;  $\tau$ , torsion; oop, out-of-plane; subscripts a and s designate antisymmetric and symmetric, respectively.

## Results

Structures of the tetrazines are given in Figure 1 with symmetry-unique internal coordinate definitions. Geometrical parameters predicted for the 1,2,3,4-tetrazine are given in Table I for the current and previous studies; Table II contains similar results for the 1,2,3,5-tetrazine (Figure 2 contains the results at the CISD/DZP level). Table III contains the relative energies of all three tetrazines for a wide range of methods. Tables IV and V contain the predicted SCF harmonic vibrational frequencies and infrared intensities for the 1,2,3,4-tetrazine and 1,2,3,5-tetrazine, respectively, at the DZP basis set level. It must be stressed that such basis sets (specifically the neglect of  $f$  functions) cannot be expected to describe well the out-of-plane frequencies for  $\pi$ -systems such as the tetrazines as demonstrated by Simandiras, Rice, Lee, Amos, and Handy.<sup>25</sup>

**Table V.** Theoretically Predicted Harmonic Vibrational Frequencies (in  $\text{cm}^{-1}$ ) and Infrared Intensities (in  $\text{km mol}^{-1}$ ) for 1,2,3,5-Tetrazine at the DZP/SCF Level

$\omega$ , $\text{cm}^{-1}$	$I$ , $\text{km mol}^{-1}$	symmetry	assignment (major components) <sup>a</sup>
1	3402	A <sub>1</sub>	$\nu_s(\text{CH})$
2	3399	B <sub>2</sub>	$\nu_s(\text{CH})$
3	1804	A <sub>1</sub>	$\nu_s(\text{C}_6\text{N}_1), \nu_s(\text{NN}), \delta_s(\text{HCN})$
4	1761	B <sub>2</sub>	$\nu_s(\text{NN}), \nu_s(\text{N}_5\text{C}_6)$
5	1567	A <sub>1</sub>	$\nu_s(\text{C}_6\text{N}_1), \nu_s(\text{NN}), \delta_s(\text{HCN})$
6	1533	B <sub>2</sub>	$\delta_s(\text{HCN})$
7	1318	B <sub>2</sub>	$\nu_s(\text{C}_6\text{N}_1), \delta_s(\text{HCN})$
8	1313	A <sub>1</sub>	$\nu_s(\text{N}_5\text{C}_6), \nu_s(\text{C}_6\text{N}_1), \nu_s(\text{NN}), \delta_s(\text{HCN})$
9	1242	A <sub>1</sub>	$\delta(\text{CNC}), \delta_s(\text{CNN})$
10	1147	A <sub>2</sub>	oop H
11	1134	A <sub>1</sub>	$\nu_s(\text{C}_6\text{N}_1), \nu_s(\text{NN}), \delta(\text{CNC}), \delta_s(\text{CNN}), \nu_s(\text{N}_5\text{C}_6)$
12	1071	B <sub>1</sub>	oop H
13	960	B <sub>2</sub>	$\nu_s(\text{NN}), \nu_s(\text{N}_5\text{C}_6), \nu_s(\text{C}_6\text{N}_1)$
14	865	B <sub>1</sub>	$\tau(\text{NHCN}), \tau(\text{CNHN})$
15	792	B <sub>2</sub>	$\delta_s(\text{CNN})$
16	736	A <sub>1</sub>	$\delta(\text{CNC}), \delta_s(\text{CNN})$
17	406	A <sub>2</sub>	$\tau(\text{CNHN})$
18	405	B <sub>1</sub>	$\tau(\text{CNHN})$

<sup>a</sup> Abbreviations:  $\nu$ , stretch;  $\delta$ , deformation;  $\tau$ , torsion; oop, out-of-plane; subscripts a and s designate antisymmetric and symmetric, respectively.

## Discussion

The geometries given in Tables I and II show the expected changes as the basis set is expanded and when electron correlation effects are included. For the SCF and CISD levels, increasing the basis set shortens the bond lengths but, with the addition of electron correlation at a given basis set, will increase the bond lengths. Interestingly the SCF/6-31G\* results of M6, De Paz, and Yáñez<sup>23</sup> (who report only molecular structures) are very similar to the CISD/DZP results reported here, except for the CH bond length.

For 1,2,3,4-tetrazine, bond lengths predicted by the semiempirical methods PPP and SPO<sup>18</sup> are in disagreement with the ab initio values. The CN bond length is shorter while the NN and CC bonds are a little longer. The N<sub>1</sub>N<sub>2</sub> bond length is reproduced well, however. All bond angles are close to their values for a perfect hexagonal structure, namely, 120°. The total molecular energies reported in this work are much lower ( $\approx 1$  hartree or more) than any reported previously.

For the 1,2,3,5-tetrazine system, similar descriptions of bond length changes with basis and theoretical level hold. For 1,2,3,5-tetrazine, however, the semiempirical results are in slightly better agreement with the ab initio predictions. Bond angles are again very close to 120°; however, the intraring angle at the carbon center has increased slightly to  $\approx 125^\circ$ .

The *s*-tetrazine molecule is generally assumed to be truly aromatic;<sup>11</sup> therefore, comparison between the *s*-tetrazine bond lengths and the corresponding ones in 1,2,3,4-tetrazine and 1,2,3,5-tetrazine is interesting. (The *s*-tetrazine values are given parenthetically in Tables I and II). The

(23) M6, O.; De Paz, J. L. G.; Yáñez, M. *J. Mol. Struct. (THEOCHEM)* 1987, 150, 135.

(24) Fernández Sanz, J.; Anguiano, J.; Vilarrosa, J. *J. Comp. Chem.* 1988, 9, 784.

(25) Simandiras, E. D.; Rice, J. E.; Lee, T. J.; Amos, R. D.; Handy, N. C. *J. Chem. Phys.* 1988, 88, 3187.

CH bond lengths are all slightly longer in the 1,2,3,4-tetrazine than in the *s*-tetrazine. The CN bond lengths are significantly shorter in 1,2,3,4-tetrazine, between 0.014 Å shorter at the SCF/DZ level and 0.02 Å shorter at the SCF/DZP level of theory. A major difference between the 1,2,3,4-tetrazine and the *s*-tetrazine is the number of NN bonds; 1,2,3,4-tetrazine has two different NN bonds, namely,  $r_3$  and  $r_5$  in Figure 1, having different bond lengths. The value of  $r_3$  is greater in 1,2,3,4-tetrazine (by  $\approx 0.02$  Å in all cases), whereas the value of  $r_5$  is smaller (by 0.009 Å at SCF/DZ, 0.016 Å at SCF/DZP, and 0.013 Å at CISD/DZP) than in *s*-tetrazine, and this occurs at all levels of theory. The NN bond in *s*-tetrazine has considerable double-bond character, and by inference so does  $r_5$  in 1,2,3,4-tetrazine; however, the latter molecule does display considerable alternation in NN bond lengths, i.e.,  $r_3/r_5$  at SCF/DZ is 1.338 Å/1.310 Å, at SCF/DZP is 1.314 Å/1.276 Å, and at CISD/DZP is 1.330 Å/1.297 Å. The CC bond length of  $\approx 1.40$  Å (the same as in benzene) in 1,2,3,4-tetrazine (*s*-tetrazine does not contain a CC bond) lies between the generally accepted values for CC single and double bonds, namely, 1.54 and 1.34 Å, respectively. The CN bond in 1,2,3,4-tetrazine ( $\approx 1.30$  Å) also lies between the accepted single- and double-bond lengths (accepted values 1.45 and 1.27 Å, respectively). These data suggest that the 1,2,3,4-tetrazine ring has some significant aromatic character although bond alternation is also evident.

Moving to the 1,2,3,5-tetrazine, the CH bonds are again longer than in *s*-tetrazine. For the intraring bond lengths, all values for 1,2,3,5-tetrazine are much closer to the corresponding values in *s*-tetrazine, a clear indication that the 1,2,3,5-tetrazine ring is more aromatic than the 1,2,3,4-tetrazine. In 1,2,3,5-tetrazine, slight alternation in the CN bond lengths is seen (the C–N bond in *s*-tetrazine is intermediate in length between the two distinct CN bonds in 1,2,3,5-tetrazine), but this C–N bond length difference is much smaller in the 1,2,3,5-tetrazine than in the 1,2,3,4-tetrazine. All bond length differences between the 1,2,3,5-tetrazine and the *s*-tetrazine are  $<0.01$  Å. This marked difference between the 1,2,3,4-tetrazine and 1,2,3,5-tetrazine rings is almost certainly due to the fact that the 1,2,3,4-tetrazine has four adjacent nitrogens whereas 1,2,3,5-tetrazine has three and *s*-tetrazine only two directly bonded pairs of nitrogen atoms. Therefore, the energy difference between the 1,2,3,4 and 1,2,3,5 isomers may be rationalized on aromaticity arguments; however, the energy difference between the 1,2,3,5- and *s*-tetrazine isomers cannot be explained in this manner.

Table III contains a summary of energy differences between the three tetrazines. All methods (except AM1) predict that the 1,2,3,5-tetrazine is the most stable tetra-

zine, with the 1,2,4,5- and 1,2,3,4-tetrazines successively less stable. This is somewhat noteworthy since the 1,2,4,5-tetrazine is the only tetrazine to be characterized experimentally. However, all three tetrazines are exothermic with respect to dissociation to the most stable products as seen in the  $\Delta H_d$  results using the MNDDO/1 method.<sup>21</sup> Of course this analysis neglects discussion of kinetic stability, which will play a crucial role in any stability argument. The upper limit to the experimentally determined barrier to the dissociation of the 1,2,4,5-tetrazine is  $\sim 52$  kcal mol<sup>-1</sup>.<sup>11</sup>

Harmonic vibrational frequencies and infrared frequencies are given in Tables IV and V for 1,2,3,4-tetrazine and 1,2,3,5-tetrazine, respectively. Both isomers are minima as seen in the expected 18 real frequencies. The predicted frequencies will hopefully aid future assignments of the vibrational modes of these two molecules. However, the infrared intensities show that few modes are intense; the only appreciable ones are those at 1804 cm<sup>-1</sup> (an A<sub>1</sub> ring-stretch mode including contributions from  $\nu_s(C_6N_1)$ ,  $\nu_s(NN)$ , and  $\delta_s(HCN)$ ), with an intensity of 87 km mol<sup>-1</sup> and 1761 cm<sup>-1</sup> (also a ring-stretch mode of B<sub>2</sub> symmetry  $\nu_a(NN)$  and  $\nu_a(N_5C_6)$  components), intensity 169 km mol<sup>-1</sup>, modes of 1,2,3,5-tetrazine. From earlier comparisons between theory and experiment for *s*-tetrazine, correlation effects and anharmonicity are expected to significantly reduce the SCF/DZP vibrational frequencies predicted at 1804 and 1761 cm<sup>-1</sup>. For *s*-tetrazine, the most closely analogous SCF/DZP harmonic vibrational frequencies lie 22.9% and 17.3% above the observed fundamentals.

### Conclusions

The current work has reported geometrical structures, relative energies, vibrational frequencies, and infrared intensities for the 1,2,3,4- and 1,2,3,5-tetrazine molecules, using DZ and DZP basis sets at the SCF and CISD levels of theory. Both structures are minima at the SCF level. Relative energy differences show that the 1,2,3,5-tetrazine is the lowest energy isomer at all levels of ab initio theory, with 1,2,4,5-tetrazine 8.0 kcal mol<sup>-1</sup> higher (at the CISD+Q/DZP level) and 1,2,3,4-tetrazine 22.2 kcal mol<sup>-1</sup> above the 1,2,3,5-tetrazine. The result is remarkable, given that the only well-characterized tetrazine is the 1,2,4,5 isomer.

**Acknowledgment.** This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Fundamental Interactions Branch, Grant DE-FG09-87ER13811.

**Registry No.** 1,2,3,4-Tetrazine, 290-42-6; 1,2,3,5-tetrazine, 592-59-6.