Synthesis and Properties of 1,2-Difluorodinitroethylene

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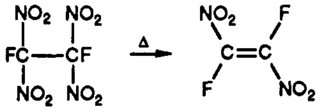
1,2-Difluorodinitroethylene was synthesized by flash vacuum pyrolysis of 1,2-difluorotetranitroethane. X-ray crystallography showed that one of the two nitro groups is out of the plane of the rest of the molecule and that the C–C double-bond distance is unusually short at 1.284 Å. 1,2-Difluorotetranitroethane reacted with alcohols to give alkyl fluoronitroacetates and with anthracene and cyclopentadiene to give Diels–Alder adducts.

There has been recent interest in the effect of electronegative substituents such as nitro[1] and fluorine[2] on the structural properties of olefins. Tetranitroethylene, the most electronegatively substituted olefin reported, is not sufficiently stable for convenient structural studies.[3] This compound could be stored only under vacuum, apparently because small amounts of nitrogen oxide otherwise resulted in rapid autocatalytic decomposition. Tetranitroethylene was synthesized by the thermal extrusion of dinitrogen tetroxide from hexanitroethane. In the present study, this novel elimination reaction has been extended to the preparation of the more stable, fully substituted olefin, 1,2-difluorodinitroethylene.

1,2-Difluorotetranitroethane[4] was prepared by the direct fluorination of the dipotassium salt of tetranitroethane in aqueous solution. Flash vacuum pyrolysis experiments were carried out on an apparatus similar to that described for the preparation of tetranitroethylene. Vaporized 1,2-difluorotetranitroethane was passed unchanged through a pyrolysis tube at 250 °C/0.5 mm. When the temperature was raised to 300 °C, approximately 25% of a new material was detected by ^{19}F NMR. The vaporization of starting material to the combustion tube was slowed by cooling the material to 0 °C, and complete conversion was obtained. The product was identified as *trans*-1,2-difluorodinitroethylene and was isolated in 92% yield as a highly volatile solid. This olefin was stable to 105 °C, well above its melting point of 39–40 °C. Unlike tetranitroethylene, 1,2-difluorodinitroethylene could be handled under normal ambient conditions; it was only slightly hygroscopic and was storable indefinitely in a freezer.



X-ray crystallographic bond lengths and angles for *trans*-1,2-difluorodinitroethylene are shown in Table I, and the geometry is illustrated in Figure 1. One of the two nitro groups shows significant deviation from coplanarity with the rest of the molecule with the average value of the four torsion angles involving the C(1)–N(1) bond being 14.3°. Similar averaging gives 0.6° for the other nitro group and 0.8° for the C(1)–C(2) twist.

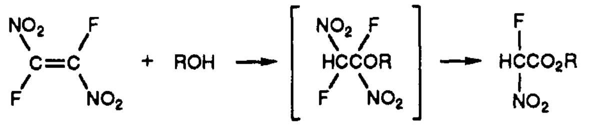
Table I. Bond Lengths (Å) and Angles (deg) for *trans*-1,2-Difluorodinitroethylene

	Bond Length		
C(1)–F(1)	1.311 (5)	C(1)–N(1)	1.476 (5)
C(1)–C(2)	1.284 (6)	N(1)–O(1A)	1.206 (5)
N(1)–O(1B)	1.208 (5)	C(2)–F(2)	1.327 (5)
C(2)–N(2)	1.476 (5)	N(2)–O(2A)	1.208 (5)
N(2)–O(2B)	1.208 (5)		
	Bond Angle		
F(1)–C(1)–N(1)	113.2 (3)	F(1)–C(1)–C(2)	123.6 (4)
N(1)–C(1)–C(2)	123.2 (4)	C(1)–N(1)–O(1B)	119.8 (3)
C(1)–N(1)–O(1B)	114.2 (3)	O(1A)–N(1)–O(1A)	126.0 (3)
C(1)–C(2)–F(2)	122.6 (4)	C(1)–C(2)–N(2)	124.6 (4)
F(2)–C(2)–N(2)	112.8 (3)	O(2A)–N(2)–O(2B)	127.0 (3)
C(2)–N(2)–O(2B)	118.4 (3)	O(2A)–N(2)–C(2)	114.6 (3)

The C–N bond distances for both nitro groups are nearly identical (1.476 Å) and are similar to those reported for nitroethylene (1.45 Å). The C–C double-bond distance is unusually short at 1.284 Å. By comparison, the double-bond distance for tetracyanoethylene is 1.35 Å and that for tetrafluoroethylene, 1.311 Å.

The ^{13}C NMR spectrum (Figure 2) is anomalous, showing a 2 × 2 × 3 pattern and unexplained signals centered at δ 144.5. The coupling constants are J_{CF} = 356.8, J_{CCF} = 77.5, and J_{CN} = 17.4 Hz. The area of the central signals is approximately the difference between that of the inner and outer triplets. The largest previously reported J_{CF} for a fluoroolefin is 355 Hz for *trans*-dibromodifluoroethylene, and values of 200–300 are typical. The ^{19}F NMR spectrum of the material showed only a singlet at δ −119.1, with no evidence of cis–trans isomers. The ^{14}N NMR spectrum showed a singlet at δ −31.859.

The reaction of tetranitroethylene with alcohols to give alkyl dinitroacetates has been reported.[3] The products were explained on the basis of the initial formation of the unstable tetranitroethyl ethers, which underwent loss of α-nitro groups. 1,2-Difluorodinitroethylene reacted similarly with methanol, ethanol, and 2-propanol to give the corresponding fluoronitroacetates, reported previously from reactions of the alcohols with fluoronitroacetyl chloride.[5]



R = Me, Et, *i*-Pr

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[1] Politzer, P.; Bar-Adon, R. *J. Am. Chem. Soc.* **1987**, *109*, 3529. Dewar, M. J. S.; Ritchie, J. P.; Alster, J. *J. Org. Chem.* **1985**, *50*, 1031. Penner, G. H. *J. Mol. Struct.* (*Theochem*) **1986**, *137*, 121–7.

[2] Smart, B. E. In *Molecular Structure and Energetics*, Vol. 3; Liebman, J. F., Greenberg, A., Eds.; UCH: Weinheim, Germany, 1986; pp 159–172. Carlos, J. L., Jr.; Karl, R. R. Jr.; Bauer, S. H. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 177–187.

[3] Baum, K.; Tzeng, D. *J. Org. Chem.* **1985**, *50*, 2736.

[4] Eremenko, L. T.; Natsibullin, F. Ya.; Borovinskaya, I. P.; Karpova, N. D. *Izv. Akad. Nauk SSSR, Ser Khim.* **1968**, 431.

[5] Martynov, I. V.; Krugylak, Yu. L. *Zh. Obshch. Khim.* **1965**, *35*, 967.

0022-3263/91/1956-0537$02.50/0

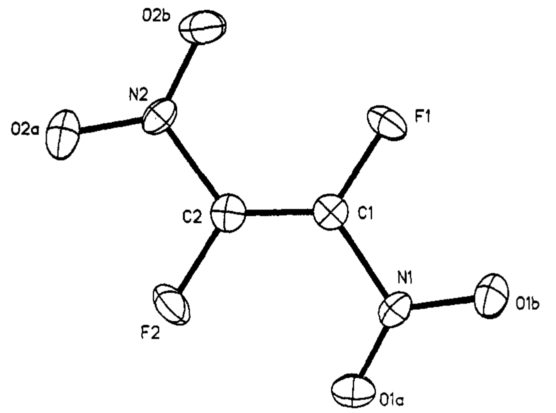

Figure 1. X-ray structure of *trans*-1,2-difluorodinitroethylene.

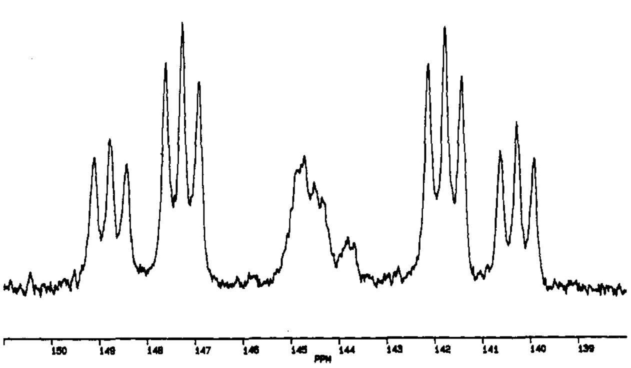

Figure 2. ^{13}C NMR spectrum of *trans*-1,2-difluorodinitroethylene.

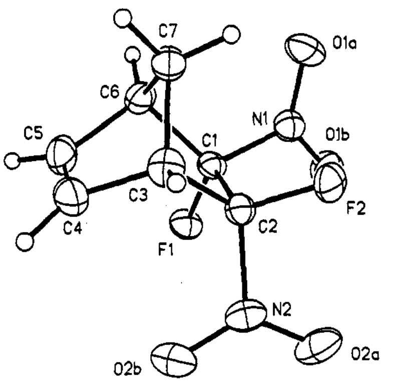

Figure 3. X-ray structure of *endo*-5,*exo*-6-difluoro-5,6-dinitrobicyclo[2.2.1]hept-2-ene.

Diels–Alder reactions of difluorodinitroethylene were also examined. Tetranitroethylene was previously shown to be an extremely reactive dienophile in Diels–Alder reactions, approximately an order of magnitude more reactive than tetracyanoethylene.[3] Its reaction with anthracene was essentially instant at ambient temperature. By contrast, the reaction of 1,2-difluorodinitroethylene with anthracene in refluxing benzene was found to give a 47% yield in 4 h of the expected adduct, 11,12-difluoro-11,12-dinitro-9,10-dihydro-9,10-ethanoanthracene, isolated as the benzene monosolvate. The reaction of 1,2-difluorodinitroethylene with cyclopentadiene at ambient temperature in methylene chloride gave *endo*-5,*exo*-6-difluoro-5,6-dinitrobicyclo[2.2.1]hept-2-ene in 49% yield. The crystallographic data and structure of this adduct are shown in Table II and Figure 3, respectively.

Table II. Bond Lengths (Å) and Angles (deg) for *endo*-5,*exo*-6-Difluoro-5,6-dinitrobicyclo[2.2.1]hept-2-ene

	Bond Length		
C(1)–F(1)	1.356 (5)	C(1)–N(1)	1.526 (6)
C(1)–C(2)	1.573 (6)	C(1)–C(6)	1.524 (6)
N(1)–O(1A)	1.207 (6)	N(1)–O(1B)	1.188 (5)
C(2)–F(2)	1.358 (5)	C(2)–N(2)	1.523 (6)
C(2)–C(3)	1.533 (6)	N(2)–O(2A)	1.200 (5)
N(2)–O(2B)	1.212 (6)	C(3)–C(4)	1.492 (7)
C(3)–C(7)	1.542 (7)	C(4)–C(5)	1.276 (8)
C(5)–C(6)	1.482 (7)	C(6)–C(7)	1.552 (7)
	Bond Angle		
F(1)–C(1)–N(1)	104.4 (3)	F(1)–C(1)–C(2)	111.3 (3)
N(1)–C(1)–C(2)	109.3 (3)	F(1)–C(1)–C(6)	114.6 (3)
N(1)–C(1)–C(6)	114.1 (3)	C(2)–C(1)–C(6)	103.1 (3)
C(1)–N(1)–O(1A)	117.3 (4)	C(1)–N(1)–O(1B)	117.6 (4)
O(1A)–N(1)–O(1B)	125.1 (4)	C(1)–C(2)–F(2)	110.2 (3)
C(1)–C(2)–N(2)	110.4 (3)	F(2)–C(2)–N(2)	104.6 (3)
C(1)–C(2)–C(3)	102.5 (3)	F(2)–C(2)–C(3)	110.5 (4)
N(2)–C(2)–C(3)	118.6 (4)	C(2)–N(2)–O(2A)	117.2 (4)
C(2)–N(2)–O(2B)	116.6 (4)	O(2A)–N(2)–O(2B)	126.1 (4)
C(2)–C(3)–C(4)	107.5 (4)	C(2)–C(3)–C(7)	98.4 (3)
C(4)–C(3)–C(7)	98.9 (4)	C(3)–C(4)–C(5)	109.4 (5)
C(4)–C(5)–C(6)	109.2 (5)	C(1)–C(6)–C(5)	103.3 (4)
C(1)–C(6)–C(7)	101.2 (3)	C(5)–C(6)–C(7)	99.0 (4)
C(3)–C(7)–C(6)	93.8 (4)		

Experimental Section

Elemental analyses were obtained from Galbraith Laboratories. Melting points are uncorrected. ^{1}H and ^{19}F NMR spectra were obtained on a Varian T-60 spectrometer and ^{13}C NMR spectra on a Bruker AC200 spectrometer in $CDCl_3$. Chemical shifts are in ppm relative to TMS or $FCCl_3$. IR spectra were obtained in CH_2Cl_2 on a Perkin-Elmer 700 spectrometer. *Polynitro compounds are potentially explosive and proper shielding should be used.*

***trans*-1,2-Difluorodinitroethylene.** A 10-mL flask containing 1,2-difluorotetranitroethane (1.58 g, 6.42 mmol) was connected in series to a horizontal 1.25 cm × 45 cm quartz tube, two traps, and a vacuum system. The flask and traps were cooled with baths at 0 °C, −20 °C, and −78 °C, respectively, the quartz tube was heated at 300 °C with a tube furnace, and the system was evacuated to 0.5 mmHg. After 20 min the starting material had evaporated. The system was vented to the atmosphere, and the −20 °C trap was warmed to ambient temperature to allow evaporation of a small amount of N_2O_4. This trap was found to contain 0.91 g (92%) of *trans*-1,2-difluorodinitroethylene, a highly volatile, pale yellow solid, mp (DSC) 39–40 °C sub, 105 °C dec: IR 1575, 1340, 950 cm^{-1}; ^{13}C NMR δ 146.1 (2 × 2 × 3, J = 356.8, 77.5, 17.4 Hz and asym multiplet at 144.5); ^{19}F NMR δ −119.1 (s, 17 Hz at $^1/_2$ height); ^{14}N NMR δ −31.86 (s, 10 Hz at $^1/_2$ height). Anal. Calcd for $C_2F_2N_2O_4$: C, 15.59; F, 24.67. Found: C, 15.43; F, 24.47.

Isopropyl Fluoronitroacetate. A solution of 1,2-difluorodinitroethylene (1.42 g, 9.22 mmol) in 2-propanol (100 mL) was refluxed for 3 h. The solvent was evaporated and the residue distilled to give 0.38 g (25%) of isopropyl fluoronitroacetate, bp 87–89 °C (42 mmHg) [lit.[5] 72 °C (9 mm)]: IR (CCl_4) 1720, 1590 cm^{-1}; ^{1}H NMR δ 5.90 (d, J = 46 Hz, 1 H), 5.15 (sept, 1 H, J = 6 Hz), 1.38 (d, 6 H, J = 6 Hz); ^{19}F NMR δ −140.5 (d, J = 46 Hz). Anal. Calcd for $C_5H_8FNO_4$: C, 36.37; H, 4.88; F, 11.51; N, 8.48. Found: C, 36.31; H, 4.87; F, 11.64; N, 8.25.

Ethyl Fluoronitroacetate. The reaction of 1,2-difluorodinitroethylene (0.807 g, 5.24 mmol) with ethanol (100 mL) by the above procedure gave ethyl fluoronitroacetate (0.273 g, 34.5%), bp 85 °C [lit.[5] 74 °C (12 mmHg)]: IR (CCl_4) 1725, 1590 cm^{-1}; ^{1}H NMR δ 1.2 (t, J = 7 Hz, 3 H), 3.7 (q, 2 H, J = 7 Hz), 5.80 (d, 1 H, J = 46 Hz); ^{19}F NMR δ −144 (d, J = 46 Hz).

Methyl Fluoronitroacetate. The reaction of 1,2-difluorodinitroethylene (0.788 g, 5.12 mmol) with methanol (100 mL) by the above procedure gave methyl fluoronitroacetate (0.202 g, 29%), bp 88–92 °C [lit.[5] 85 °C (30 mmHg)]: IR (CCl_4) 1720, 1590 cm^{-1}; ^{1}H NMR δ 4.0 (s, 3 H), 6.15 (d, 1 H, J = 46 Hz); ^{19}F NMR δ −1.44 (d, J = 46 Hz).

11,12-Difluoro-11,12-dinitro-9,10-dihydro-9,10-ethanoanthracene. A solution of 1,2-difluorodinitroethylene (0.080 g, 0.52 mmol) and anthracene (0.200 g, 1.12 mmol) in benzene (12 mL) was refluxed for 4 h and cooled to room temperature. A white solid separated and was recrystallized from benzene to give 0.099 g (47%) of 11,12-difluoro-11,12-dinitro-9,10-dihydro-9,10-ethanoanthracene benzene monosolvate, mp 192–193 °C: IR 1590,

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1350 cm^{-1}; ^{1}H NMR δ 7.2 (m, 14 H), 4.9 (m, 2 H); ^{19}F NMR δ −121.5 (s). Anal. Calcd for $C_{22}H_{16}F_2N_2O_4$: 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-difluorodinitroethylene (0.299 g, 1.94 mmol) and freshly distilled cyclopentadiene (1.5 g, 23 mmol) in CH_2Cl_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, Ch_2Cl_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 cm^{-1}; ^{1}H NMR δ 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}F NMR δ −121.03 (bs). Anal. Calcd for $C_7H_6F_2N_2O_4$: 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: $C_2F_2N_2O_4$, $M_r = 154.0$, orthorhombic space group *Pbca*, $a = 9.375$ (2), $b = 0.122$ (3), and $c = 10.505$ (3) Å, $V = 996.8$ (4) Å^3, $Z = 8$, $D_X = 2.053$ Mg m^{-1}, λ(Mo Kα) = 0.71073 Å, $\mu = 0.22$ mm^{-1}, $F(000) = 608$, data collection $T = 201$ K, final $R = 0.055$, w$R = 0.066$ 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 $22 < 2\theta < 39°$ were used for determing lattice parameters. ($\sin(\theta)/\lambda_{max} = 0.54$ Å^{-1}; 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 ±2.5% over data collection, $\theta/2\theta$ mode, scan width $[2\theta(K_{\alpha1}) - 0.9]$ to $[2\theta(K_{\alpha2}) + 0.9]°$, 2θ scan rate 60.0° min^{-1} (rapid due to volatile crystal); 1534 reflections measured, 654 unique, 587 observed with $F_o > 3\sigma(F_o)$; $R_{int} = 0.042$. 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 $F_c{}^t$mo $= F_c/[1.0 + 0.002(p)F_o{}^2/\sin(2\theta)]^{0.25}$. There were 92 parameters refined: all atom coordinates, anisotropic temperature parameters for nonhydrogen atoms; the hydrogen atoms were assigned fixed isotropic thermal parameters. $(\Delta/\sigma)_{max} = 0.01$, $R = 0.055$, w$R = 0.066$, $S = 2.88$. Final difference Fourier excursions 0.51 and −0.28 e Å^{-3}. Atomic scattering factors from *International Tables for Crystallography*.[6] The programs used for structure solution, refining, and plotting are part of SHELXTL.[7,8]

X-ray analysis of *endo*-5,*exo*-6-difluoro-5,6-dinitrobicyclo[2.2.1]hept-2-ene: $C_7H_6F_2N_2O_4$, $M_r = 220.14$, orthorhombic space group $P22_12_1$, $a = 6.033$ (3), $b = 11.629$ (4), and $c = 12.501$ (4) Å, $V = 877.1$ (3) Å^3, $Z = 4$, $D_X = 1.667$ Mg m-1, λ(Cu Kα) = 1.54183 Å, $\mu = 1.42$ mm^{-1}, $F(000) = 448$, data collection $T = 295$ K, final $R = 0.045$, w$R = 0.047$ 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 $45 < 2\sigma < 88°$ were used for determining lattice parameters. $(\sin(\theta)/\lambda)_{max} = 0.56$ Å^{-1}; 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 ±15% over data collection, $\theta/2\theta$ mode, scan width $[2\theta(K_{\alpha1}) - 1.0]$ to $[2\theta(K_{\alpha2}) + 1.0]°$, 2σ scan rate 60° min^{-1} (rapid due to volatile crystal, full data set collected in 4 h); 855 reflections measured, 841 unique, 736 observed with $F_o > 3\sigma(F_o)$; $R_{int} = 0.030$. 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 $F_c{}^* = F_c/[1.0 + 0.002(p)F_o{}^2/\sin(2\sigma)]^{0.25}$. 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. $(\Delta/\sigma)_{max} = 0.04$, $R = 0.045$, w$R = 0.047$, $S = 1.41$. Final difference Fourier excursions 0.16 and −0.18 e Å^{-3}. Atomic scattering factors from *International Tables for Crystallography*.[6] The programs used for structure solution, refining, and plotting are part of SHELXTL.[7,8]

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

(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

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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^{-1} 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 nitrogen atoms), only the 1,2,4,5-tetrazine (also called *s*-tetrazine) has been unambiguously characterized experimentally.[1-3] The other two isomers, 1,2,3,4- and 1,2,3,5-

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† 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.

0022-3263/91/1956-0539$02.50/0 © 1991 American Chemical Society