DFT and G2MP2 Calculations of the N-N Bond Dissociation Enthalpies and Enthalpies of Formation of Hydrazine, Monomethylhydrazine and Symmetrical and Unsymmetrical Dimethylhydrazine

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Dedicated to Professor Ingo-Peter Lorenz on the occasion of his 60th birthday

In a combined DFT (B3LYP) and G2MP2 theoretical study the following enthalpies of formation ($\Delta H^\circ{}_f$) and bond dissociation enthalpies (*BDE*) for hydrazine, methylhydrazine (MMH), 1,1-dimethylhydrazine (UDMH) and 1,2-dimethylhydrazine (SDMH) were determined: *BDE*/kJ mol^{-1}: N_2H_4, 278 ± 4; MMH, 272 ± 4; UDMH, 259 ± 12; SDMH, 272 ± 12. $\Delta H^\circ{}_f$/kJ mol^{-1}: N_2H_4, 95 ± 6; MMH, 94 ± 4; UDMH, 80 ± 4; SDMH, 91 ± 4. The bond enthalpy for the N-N bond in hydrazine amounts to *BE* (N-N, $H_2N - NH_2$) $= 159 \pm 4$ kJ mol^{-1}.

Key words: Dimethylhydrazine, Hydrazine, MMH, Monomethylhydrazine, N-N Bond Dissociation Energies, UDMH

Introduction

Hydrazine and its methyl derivatives are extensively used as fuels in rocket engines [1]. The development of new hypergolic propellants on the basis of hydrazine gels requires reliable thermodynamic data for the individual components. Since there are large discrepancies for the reported literature values for the enthalpies of formation ($\Delta H^\circ{}_f$) of hydrazine (N_2H_4), monomethylhydrazine (MMH), 1,1-dimethylhydrazine (UDMH) and 1,2-dimethylhydrazine (SDMH) (Table 1), we report here the computed N-N bond dissociation enthalpies (*BDE*) and $\Delta H^\circ{}_f$ values for hydrazine, MMH, UDMH and SDMH on the basis of DFT (density functional theory) and G2MP2 calculations.

It has to be stressed, that here we report on the computed N-N bond dissociation enthalpies (*BDE*) and not on the bond enthalpy terms (*BE*). For hydrazine, for example, the bond dissociation enthalpy is the enthalpy $\Delta H^\circ{}_R$ of the following reaction (1) forming two radicals $H_2N^\bullet$ in their equilibrium configuration.

$$H_2N\text{-}NH_2\,(g) \rightarrow 2\,H_2N^\bullet\,(g) \qquad (1)$$

The N-N bond enthalpy (*BE*) for hydrazine is the enthalpy $\Delta H^\circ{}_R$ of reaction (2) minus four times the average bond enthalpy of an N-H bond. The recommended literature value for the N-N bond enthalpy in hydrazine is approximately 159 kJ mol^{-1} [12].

$$H_2N\text{-}NH_2\,(g) \rightarrow 2\,N\,(g) + 4\,H\,(g) \qquad (2)$$

Methods

The Gaussian G98W program was used for all MO structure and frequency calculations [18]. All structures were fully optimized within the symmetry constraints indicated in Table 2, and the frequencies (*NIMAG* = 0)* and zero point energies (zpe) were calculated at the B3LYP† hybrid DFT‡ level of theory (Table 2) [19 – 22] using a standard dou-

*NIMAG: number of imaginary frequencies.

†B3LYP: hybrid HF-DFT method of Becke, using Becke's gradient correction to the exchange functional and Lee, Yang, Parr's (LYP) correlation functional and Vosko, Wilk, Nusair's (VWN) local correlation functional.

‡DFT: density functional theory.

Table 1. Literature values for the enthalpies of formation and the bond dissociation enthalpies for hydrazine, MMH, UDMH and SDMH.

	N_2H_4	MMH	UDMH	SDMH
ΔH°_f (g) / kJ mol^{-1}	90 [1] 95 [2] 151 ± 8 [3] 50 [4] 95 [14]	92 [1] 94 [4 – 6] 95 [15]	84 [1] 83 [5 – 8] 84 [15]	92 [15]
ΔH°_{vap} / kJ mol^{-1}	45 [2] 39 [1]	40 [5, 6] 37 [1]	33 [1] 35 [5, 8]	39 [5, 9]
BDE / kJ mol^{-1}	exp: 276 ± 8 [10], 296 ± 8[16,17]; calcd: 293 [11], 247 [12], 247 ± 12 [13] 251 [14]	exp: 268 ± 8 [10], calcd: 276[11]	exp: 247 ± 8 [10], calcd: 255[11]	

ble zeta basis set (6-31G(d)[§]) [23, 24]. The B3LYP/6-31G(d) method reproduces the experimental structures for all known hydrazine derivatives very well (for example N_2H_4, exptl.(gas phase)/calcd.: *d*(NN) 1.45 Å/1.437 Å, *d*(NH) 1.02 Å/1.017 Å, torsion angle 91°/90.5° [14]). Single-point energies were obtained using an extended 6-311+G(3df,2pd)[¶] basis set at the B3LYP/6-311+G(3df,2pd)//B3LYP/6-31G(d) level of theory [25, 26]. This procedure has been recommended by Foresman and Frisch [27] as the best level of theory for highly accurate energies, only exceeded (in terms of energy accuracy) by the G1 and G2[‖] methods. Therefore, in order to accurately compute the thermodynamic properties, especially the enthalpy values, G2MP2[‖]calculations were performed at the B3LYP/6-31G(d) optimized geometries [28, 29]. The mean absolute deviation for the total energy at this level (G2) of theory has been stated as 1 – 2 kcal mol^{-1} [27].

Results and Discussion

Bond dissociation enthalpies

The total electronic energies and zero point energies of hydrazine, MMH, UDMH and SDMH were calculated at the DFT level and the results are summarized in Table 2.

[§]6-31G(d): Pople polarized valence double-zeta basis set of gaussian functions.

[¶]6-311+G(3df,2pd): Pople polarized valence triple-zeta basis set of gaussian functions, augmented with one diffuse function.

[‖]G2MP2: Gaussian 2 – Møller-Plesset second order perturbation method (uses MP2 instead of MP4 for the basis set extension corrections); Gaussian 2 stands for a defined procedure for computing very accurate energies.

Table 2. Computational results. Total electronic energies ($-E$) at B3LYP/6-311+G(3df,2pd)//B3LYP/6-31G(d) level of theory, zero point energies (*zpe*) at B3LYP/6-31G(d) level of theory and G2MP2 enthalpies (*H*). 1 atomic energy unit = 1 a. u. = 1 Hartree = $4.35981 \cdot 10^{-18}$ J ≙ $2.6254972 \cdot 10^6$ J mol^{-1}.

	Point group	$-E^{B3LYP}$ / a. u.	zpe^{B3LYP} / kJ mol^{-1}	H^{G2MP2} / a. u.
N_2H_4	C_2	111.918707	141	−111.673443
$CH_3HN\text{-}NH_2$	C_1	151.239200	215	−150.889935
$(CH_3)_2N\text{-}NH_2$	C_1	190.562203	288	−190.111602
$CH_3HN\text{-}NHCH_3$	C_1	190.559822	290	−190.106779
NH_2	C_{2v}	55.904955	50	−55.783338
CH_3NH	C_1	95.232885	129	−95.001570
$(CH_3)_2N$	C_1	134.561453	204	−134.224068
N_2	$D_{\infty h}$	109.566808	15	−109.386179
H_2	$D_{\infty h}$	1.180012	27	−1.163046
CH_4	T_d	40.537470	119	−40.405849
H	K_h^a	0.502156	–	−0.497639
N	K_h^a	54.600723	–	−54.513945
NH_3	C_{3v}	56.587379	91	−56.453361

[a] The point group "K_h" symbolizes spherical symmetry (see ref. [14], p. 175 – 178).

Table 3. Calculated dissociation energies ($\Delta E^{el,B3LYP}$) and bond dissociation enthalpies at B3LYP (BDE^{B3LYP}) an G2MP2 level of theory (BDE^{G2MP2}).

Eq.	Hydrazine Derivative	ΔE^{el} / kJ mol^{-1}	BDE^{B3LYP} / kJ mol^{-1}	BDE^{G2MP2}/ kJ mol^{-1}
3	$H_2N\text{-}NH_2$	285	254	280
4	$CH_3HN\text{-}NH_2$	266	240	276
5	$(CH_3)_2N\text{-}NH_2$	251	227	273
6	$CH_3HN\text{-}NHCH_3$	247	225	272

The N-N dissociation energies (ΔE^{el}) for hydrazine, MMH, UDMH and SDMH were calculated according to equations (3) – (6) using the energies given in Table 2 and are summarized in Table 3.

$$H_2N\text{-}NH_2\,(g) \rightarrow 2\ {}^{\bullet}NH_2\,(g) \quad (3)$$

$$CH_3HN\text{-}NH_2\,(g) \rightarrow CH_3NH^{\bullet}\,(g) + {}^{\bullet}NH_2\,(g) \quad (4)$$

$$(CH_3)_2N\text{-}NH_2\,(g) \rightarrow (CH_3)_2N^{\bullet}\,(g) + {}^{\bullet}NH_2\,(g) \quad (5)$$

$$CH_3HN\text{-}NHCH_3\,(g) \rightarrow 2CH_3NH^{\bullet}\,(g) \quad (6)$$

After corrections for the zero point energies, the work term (pΔV = 1 RT, with 1 RT = 2.479 kJ mol^{-1} at 298.15 K), the translational energy (ΔU^{tr} = 1.5 RT) and the rotational energy (ΔU^{rot} = 1.5 RT), the ΔE^{el} values were converted into the reaction enthalpies of reactions (1) – (4) which are identical to the bond dissociation enthalpies (*BDE*) of hydrazine, MMH, UDMH and SDMH (Table 3) [30]. Table 3 also contains the

Table 4. Reaction energies and enthalpies of reactions (5) - (8).

Eq.	ΔE^{el} / kJ mol^{-1}	ΔH^{B3LYP} / kJ mol^{-1}	ΔH^{G2MP2} / kJ mol^{-1}
7	−21	−78	−102
8	−118	−156	−171
9	−209	−226	−226
10	−215	−234	−239

BDE values of hydrazine, MMH, UDMH and SDMH, which were computed at the G2MP2 level of theory.

Enthalpies of formation

The DFT computed electronic energies and G2MP2 computed enthalpies (Table 2) were also used to calculate the reaction enthalpies of the hypothetical reactions (7) – (10) in order to estimate the standard enthalpies of formation of hydrazine, MMH, UDMH and SDMH [30] (Table 4).

$$H_2N\text{-}NH_2\,(g) \rightarrow N_2\,(g) + 2\,H_2\,(g) \quad (7)$$

$$CH_3HN\text{-}NH_2\,(g) \rightarrow CH_4\,(g) + N_2\,(g) + H_2\,(g) \quad (8)$$

$$(CH_3)_2N\text{-}NH_2\,(g) \rightarrow 2\,CH_4\,(g) + N_2\,(g) \quad (9)$$

$$CH_3HN\text{-}NHCH_3\,(g) \rightarrow 2\,CH_4\,(g) + N_2\,(g) \quad (10)$$

With the well established standard enthalpy of formation (ΔH°_f) of methane (ΔH°_f,CH_4(g) = -75 ± 1 kJ mol^{-1}) [2, 31] one can now calculate the standard enthalpies of formation of hydrazine, MMH, UDMH and SDMH in the gas phase at two levels of theory:

B3LYP/6-311+G(3df,2pd)//B3LYP/6-31G(d) level of theory:**

ΔH°_f(H_2N-NH_2, g) = +78 kJ mol^{-1}
ΔH°_f(CH_3HN-NH_2, g) = +81 kJ mol^{-1}
ΔH°_f($(CH_3)_2N$-NH_2, g) = +77 kJ mol^{-1}
ΔH°_f(CH_3HN-$NHCH_3$, g) = +84 kJ mol^{-1};

G2MP2//B3LYP/6-31G(d) level of theory:**

ΔH°_f(H_2N-NH_2, g) = +102 kJ mol^{-1}
ΔH°_f(CH_3HN-NH_2, g) = +96 kJ mol^{-1}
ΔH°_f($(CH_3)_2N$-NH_2, g) = +77 kJ mol^{-1}
ΔH°_f(CH_3HN-$NHCH_3$, g) = +89 kJ mol^{-1}.

**ΔH(T): reaction enthalpy, for a precise definition see ref. [30], $\Delta H = \Delta U + p\Delta V$; $\Delta H(T) = \Delta U(T) + \Sigma \nu_i$ RT; $\Delta U(T) = \Delta U^{trans}(T) + \Delta U^{rot}(T) + \Delta U^{vib}(T) + \Delta U^{el}(T)$.

Table 5. Experimental and computed values for the enthalpies of formation and the bond dissociation enthalpies for hydrazine, MMH, UDMH and SDMH.

	N_2H_4	**MMH**	**UDMH**	**SDMH**
ΔH°_f (g) / kJ mol^{-1} (exptl.)	90 [1] 95 [2]	92 [1]	84 [1]	92 [15]
ΔH°_f (g) / kJ mol^{-1} (B3LYP [a], G2MP2[b])	78[a] 102[b]	81[a] 96[b]	77[a] 77[b]	84[a] 89[b]
BDE / kJ mol^{-1} (exptl)	276 ± 8 [10]	268 ± 8 [10]	247 ± 8 [10]	–
BDE / kJ mol^{-1} (B3LYP[a], G2MP2[b])	254[a] 280[b]	240[a] 276[b]	227[a] 273[b]	225[a] 272[b]

[a] This work at B3LYP/6-311+G(3df,2pd)//B3LYP/6-31G(d) level of theory; [b] this work at G2MP2 level of theory.

N-N Bond enthalpy in H_2N-NH_2

The N-N bond enthalpy in hydrazine was estimated on the basis of the total dissociation of H_2N-NH_2 into the atoms (eq. (11), *cf.* Table 2).

$$H_2N\text{-}NH_2\,(g) \rightarrow 2\,N\,(g) + 4\,H\,(g) \quad (11)$$

The energy of reaction (11) ($\Delta E^{el,B3LYP}$ = +1859 kJ mol^{-1}) was converted after corrections for (Δzpe = −141 kJ mol^{-1}), the work term ($p\Delta V$ = 5 RT), the translational energy (ΔU^{tr} = 7.5 RT) and the rotational energy (ΔU^{rot} = −1.5 RT) into the reaction enthalpy of reaction (11) [30], $\Delta H^{B3LYP}(9)$ = +1746 kJ mol^{-1}. If the average N-H bond enthalpy in NH_3 (eq. (12)) is taken equal to that in hydrazine, the desired value for the N-N bond enthalpy in N_2H_4 can be estimated from the energy of reaction (12), $\Delta E^{el}(10)$ = 1260 kJ mol^{-1}. [*N.B.* although the assumption that the N-H bond enthalpy in NH_3 is equal to that in N_2H_4 seems to be crude, it is usually justified to make this assumption. For a more detailed discussion see ref. [12, p. 92 – 96.]

$$NH_3\,(g) \rightarrow N\,(g) + 3\,H\,(g) \quad (12)$$

The $\Delta E^{el,B3LYP}(12)$ value was converted after corrections for (Δzpe = −91 kJ mol^{-1}), the work term ($p\Delta V = 3$ RT), the translational energy ($\Delta U^{tr} = 4.5$ RT) and the rotational energy (ΔU^{rot} = −1.5 RT) into the enthalpy of reaction (12) [30], $\Delta H^{B3LYP}(12)$ =

+1184 kJ mol^{-1}. If an average N-H bond enthalpy of 395 kJ mol^{-1} (B3LYP level of theory) is assumed for both NH_3 and N_2H_4, the N-N bond enthalpy of H_2N-NH_2 can be estimated to be BE^{B3LYP}(N-N, in N_2H_4) = 168 kJ mol^{-1}.

The same calculation using the G2MP2 obtained enthalpies (Table 2) yields a $\Delta H^{\mathrm{G2MP2}}(11)$ of +1718 kJ mol^{-1} and a $\Delta H^{\mathrm{G2MP2}}(12)$ of +1172 kJ mol^{-1}. If now an average N-H bond enthalpy of 390 kJ mol^{-1} (G2MP2 level of theory) is assumed for both NH_3 and N_2H_4, the N-N bond enthalpy of H_2N-NH_2 can be estimated to be BE^{G2MP2}(N-N, in N_2H_4) = 157 kJ mol^{-1}.

Conclusions

From the present combined DFT and G2MP2 study the following conclusions can be drawn:

(i) The DFT calculated values are in good accord, the G2MP2 computed data in excellent agreement with the most reliable reported experimental data (Table 5). The previously reported enthalpies of formation of hydrazine of 50 [4] and 151 [3] kJ mol^{-1} are clearly incorrect.

(ii) The bond dissociation enthalpies (*BDE*) for the cleavage of the N-N bond decreases in the order N_2H_4 > MMH > UDMH > SDMH.

(iii) The computed bond enthalpy (*BE*) for the N-N bond in hydrazine of 168 kJ mol^{-1} (B3LYP) and 157 kJ mol^{-1} (G2MP2) agrees very well with the literature estimate of 159 kJ mol^{-1} [12].

The authors of this contribution therefore suggest the following enthalpies of formation and the bond dissociation enthalpies for hydrazine, MMH, UDMH and SDMH as the best available values:

BDE / kJ mol^{-1}: N_2H_4, 278 ± 4; MMH, 272 ± 4; UDMH, 259 ± 12; SDMH, 272 ± 12.

$\Delta H^{\circ}{}_{\mathrm{f}}$ / kJ mol^{-1}: N_2H_4, 95 ± 6; MMH, 94 ± 4; UDMH, 80 ± 4; SDMH, 91 ± 4.

The bond enthalpy for the N-N bond in hydrazine: *BE* (N-N, H_2N-NH_2) = 159 ± 4 kJ mol^{-1}.

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[1] E. W. Schmidt, Hydrazine and its Derivatives – Preparation, Properties, Application, Vol. 1 and 2, Wiley, Chichester, New York (2001).
[2] M. W. Chase (Jr.), NIST-JANAF Thermochemical Tables, 4th edn., J. Phys. Chem. Ref. Data, Monograph 9, 1 – 1951 (1998).
[3] C. Willis, F. P. Lossing, R. A. Back, Can. J. Chem. **54**, 1 (1976).
[4] L. G. Cole, E. C. Gilbert, J. Am. Chem. Soc. **73**, 5423 (1951).
[5] V. Majer, V. Svoboda, Enthalpies of Vaporization of Organic Compounds: A Critical Review and Data Compilation, p. 300, Blackwell Scientific Publications, Oxford (1985).
[6] J. G. Aston, H. L. Finke, G. L. Janz, K. E. Russell, J. Am. Chem. Soc. **73**, 1939 (1951).
[7] T. M. Donovan, C. H. Shomate, W. R. McBride, J. Phys. Chem. **64**, 281 (1960).
[8] J. G. Aston, J. L. Wood, T. P. Zolki, J. Am. Chem. Soc. **75**, 6202 (1953).
[9] J. G. Aston, G. J. Janz, K. E. Russell, J. Am. Chem. Soc. **73**, 1943 (1951).
[10] D. F. McMillen, D. M. Golden, Ann. Rev. Phys. Chem. **33**, 493 (1982).
[11] B. S. Jursic, J. Mol. Struct. (Theochem) **366**, 103 (1996).
[12] T. M. Klapötke, I. C. Tornieporth-Oetting, Nichtmetallchemie, p. 92 – 94, VCH, Weinheim (1994).
[13] J. E. Huheey, Anorganische Chemie, p. 1071, Walter de Gruyter, Berlin (1988).
[14] A. F. Holleman, E. Wiberg, N. Wiberg, Lehrbuch der Anorganischen Chemie, 101st edn., p. 141 Walter de Gruyter, Berlin (1995).
[15] B. Ma, J.-H. Lii, K. Chen, N. L. Allinger, J. Phys. Chem. **100**, 11297 (1996).
[16] S. W. Benson, H. E. O'Neal, Kinetic Data on Gas Phase Unimolecular Reactions, National Bureau of Standards, Washington, DC, NSRDS-NBS 21 (1970).
[17] D. J. Pasto, J. Mol. Struct. **446**, 75 (1998).
[18] Gaussian 98, Revision A.3, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery (Jr.), R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng,

A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh PA (1998).

[19] C. Lee, W. Yang, R. G. Parr, Phys. Rev. **B37**, 785 (1988).

[20] A. D. Becke, Phys. Rev. **A38**, 3098 (1988).

[21] B. Miehlich, A. Savin, H. Stoll, H. Preuss, Chem. Phys. Lett. **157**, 200 (1989).

[22] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[23] A. D. McLean, G. S. Chandler, J. Chem. Phys. **72**, 5639 (1980).

[24] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, J. Chem. Phys. **72**, 650 (1980).

[25] T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. v. R. Schleyer, J. Comp. Chem. **4**, 294 (1983).

[26] M. J. Frisch, J. A. Pople, J. S. Binkley, J. Chem. Phys. **80**, 3265 (1984).

[27] J. B. Foresman, Æ. Frisch, Exploring Chemistry with Electronic Structure Methods, 2nd edn., p. 158, Gaussian, Inc., Pittsburgh (1993).

[28] L. A. Curtiss, K. Raghavachari, G. W. Trucks, J. A. Pople, J. Chem. Phys. **94**, 7221 (1991).

[29] L. A. Curtiss, K. Raghavachari, J. A. Pople, J. Chem. Phys. **98**, 1293 (1993).

[30] T. M. Klapötke, A. Schulz, R. D. Harcourt, Quantum Chemical Methods in Main-Group Chemistry, Chapter 5, Wiley, Chichester (1998).

[31] NIST Chemistry WebBook, NIST Standard Reference Database Number 69 – March, 2003 Release (2003): http://webbook.nist.gov.