Studies on Heats of Formation for Tetrazole Derivatives with Density Functional Theory B3LYP Method

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The heats of formation (HOF) for 49 tetrazole derivatives are calculated with the density functional theory (DFT) B3LYP method by means of designed isodemic and isogyric reactions. The average absolute deviation for five compounds for which the experimental HOFs are available is less than 2 kcal/mol target accuracy of G-2 theory. It has been demonstrated that for compounds involving delocalized bonds, choosing molecules containing all of the delocalized bonds as reference compounds is an appropriate approach. The calculated HOFs indicate that most neutral 2H-isomers are more stable than the corresponding 1H-isomers whereas the 1-substituted tetrazolate anions are more stable than the corresponding 2-substituted ones. Furthermore, our results consistently show that C-substituted tetrazoles are more stable than the corresponding N-substituted isomers. Our calculated heat of formation calls into question the experimental heat of formation of 2-methyltetrazole.

Introduction

Recently there has been an intense development of the chemistry of tetrazoles. The tetrazole compounds have found wide application in agriculture, medicine, biology, etc.[1] There is also a lot of work being done on the potential of tetrazoles and their metal salts to be used as explosives.[1−6] It is well known that the evaluation of explosive performances of energetic materials requires the knowledge of the heat of formation (HOF). Furthermore, HOFs, as elementary thermodynamic properties, are important and necessary for researchers. For stable compounds, of course, there are many tables that contain experimental data of HOFs. However, for energetic materials and unstable compounds, determination of the HOFs is impractical or dangerous. At this time one may calculate them from empirical models such as group additivity methods. Such methods work very well for hydrocarbons, but they often fail for other classes of compounds.[7] On the other hand, theoretical calculations of HOF have been the focus of computational chemistry and of theoretical chemistry.[8−17] Many computational methods for HOF have been proposed.[12−15,18,19] Most of them are based on the obtained total energies from ab initio calculations at higher levels. The typical methods are the Gaussian [G-1,G-2, G-2(MP2), and G-2(MP2, SVP)] series proposed by Pople and co-workers.[19] It was demonstrated that these methods are capable of computing HOF with an average error of less than 2.0 kcal/mol. However, in calculating HOFs with the G-2 theory model, one often encounters the problem of computational time and disk space which results from the goal of obtaining the highly accurate total energy because the conventional ab initio electron correlation methods, such as QCISD(T) and MP2, are computationally expensive. Nowadays density functional theory (DFT) methods have become a popular way of dealing with various chemical problems where the commonly used ab initio methods are too expensive. Moreover, the recent work shows that as long as the DFT methods used are suitable for the system investigated, can one obtain satisfactory HOFs.[13,15,17]

The isodemic way of determining heats of formation for molecular species has been very successful.[20] The isodemic reaction is a kind of process in which the number of each kind of formal bond is conserved and the isogyric reaction is a process in which the number of electron pairs is conserved.[20] Calculation errors inherent in the individual reactant and product molecules in the reactions are largely reduced. Thus, the calculated deviation of HOF will be small. Usually isodemic reaction processes are used with application of the bond separation reaction rule. The molecule is broken down into a set of two heavy-atom molecules containing the same component bonds.[13] This is not an easy task for molecules with delocalized bonds. Since all of the compounds investigated here contain delocalized bonds, an appropriate approach should be adopted.

To our knowledge, no theoretically computed HOFs for tetrazole derivatives with DFT method, other than our recent work,[17] are reported, though experimental HOFs for some tetrazole compounds were presented.[21−23] We only found several semiempirical MO calculations[24−26] in this subject. Series investigations[17,27−35] on tetrazole derivatives show that electron correlation effects in tetrazoles are great. Calculations including electron correlation correction are important for obtaining more accurate energies of tetrazole compounds. In this paper we are going to present our theoretically computed HOFs with density functional theory B3LYP method for 49 tetrazole derivatives by means of designed isodemic and isogyric reactions. The calculated results have been discussed concerning relative stability of the titled compounds.

Calculation Details

As pointed out above, tetrazole compounds contain delocalized bonds. The conventional bond separation reaction rule

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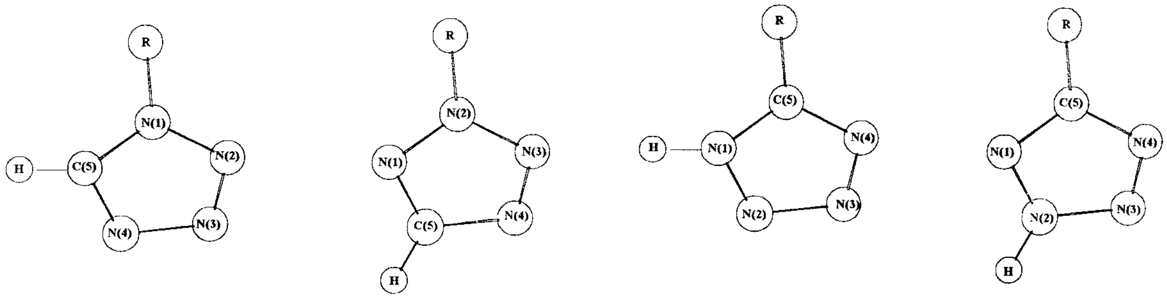
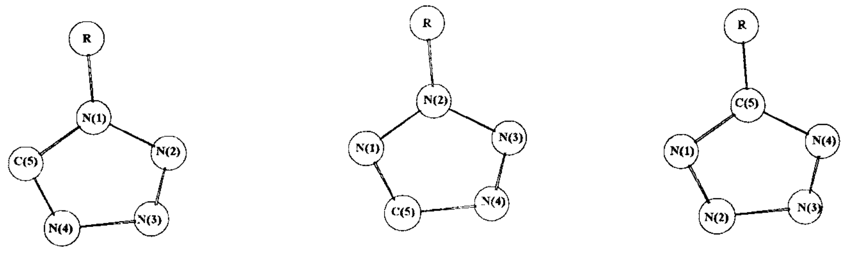


1-substituted tetrazoles 2-substituted tetrazoles 5-substituted 1H-tetrazoles 5-substituted 2H-tetrazoles



1-substituted tetrazolate anions 2-substituted tetrazolate anions 5-substituted tetrazolate anions

Figure 1. Tetrazole Derivatives and Tetrazolate Anions (R = $-CH_3$, $-NH_2$, $-CN$, $-OH$, $-NHNH_2$, $-Cl$, $-NHNO_2$).

cannot be applied to them. To solve this problem, in this paper we do not break down the tetrazole skeleton ring into a set of two heavy-atom molecules. To be specific, we take 1H-tetrazole and 2H-tetrazole as the reference compounds. The reliability of this approach has been confirmed by our recent work.[17]

Basis sets used in the calculation of total energies have important effects in both the calculated HOFs and the CPU time. One way of reducing the CPU time in calculating HOFs with the G-2 theory is to use a smaller basis set, as in G2(MP2,SVP) and G2(MP2,VP). Diffuse functions have long been known to be important in the description of anions and systems involving lone pair electrons.[36−38] However, studies[39,40] show that the total energies of tetrazole compounds calculated with B3LYP method at 6-31G* basis set level are as accurate as the high level ab initio[QCISD(T)/6-311++G(3df, 2pd)] results, though tetrazole compounds are systems involving lone pair electrons. The calculated HOF (355.9kJ/mol) of 2-methyl-5-ethenyl-tetrazole (2M-5ETz) from B3LYP/6-31G* total energy is in very good agreement with the experimental data (354.0 kJ/mol).[17] To check the effects of basis set on the calculation results, we have compared the HOFs obtained with different basis sets (6-31G* and 6-31+G*). It was found that for neutrals the HOFs obtained at B3LYP/6-31G* are very close to those at the B3LYP/6-31+G* level. For example, the average absolute deviation of the calculated HOFs from different basis sets for four neutral methyl derivatives of tetrazole is only 0.34 kcal/mol. However, for tetrazolate anions the calculated HOFs with 6-31+G*[41](diffuse basis sets) are about 10 to 20 kcal/mol less than those with 6-31G* basis set, which indicates that diffuse basis sets are important for anions. As saving the CPU time is one goal of ours, thus in this paper we approach the HOFs of 28 neutral tetrazole derivatives at the B3LYP/6-31G* level, while for the 21 tetrazolate anions we use the 6-31+G* diffuse basis set.

TABLE 1: Numbering of the Titled Compounds

name	no.	name	no.
1-methyltetrazole	**1**	1-hydroxyl-tetrazole anion	**26**
2-methyltetrazole	**2**	2-hydroxyl-tetrazole anion	**27**
5-methyl-1H-tetrazole	**3**	5-hydroxyl-tetrazole anion	**28**
5-methyl-2H-tetrazole	**4**	1-hydrazinotetrazole	**29**
1-methyl-tetrazole anion	**5**	2-hydrazinotetrazole	**30**
2-methyl-tetrazole anion	**6**	5-hydrazino-1H-tetrazole	**31**
5-methyl-tetrazole anion	**7**	5-hydrazino-2H-tetrazole	**32**
1-aminotetrazole	**8**	1-hydrazino-tetrazole anion	**33**
2-aminotetrazole	**9**	2-hydrazino-tetrazole anion	**34**
5-amino-1H-tetrazole	**10**	5-hydrazino-tetrazole anion	**35**
5-amino-2H-tetrazole	**11**	1-chlorotetrazole	**36**
1-amino-tetrazole anion	**12**	2-chlorotetrazole	**37**
2-amino-tetrazole anion	**13**	5-chloro-1H-tetrazole	**38**
5-amino-tetrazole anion	**14**	5-chloro-2H-tetrazole	**39**
1-cyanotetrazole	**15**	1-chloro-tetrazole anion	**40**
2-cyanotetrazole	**16**	2-chloro-tetrazole anion	**41**
5-cyano-1H-tetrazole	**17**	5-chloro-tetrazole anion	**42**
5-cyano-2H-tetrazole	**18**	1-nitraminotetrazole	**43**
1-cyano-tetrazole anion	**19**	2-nitraminotetrazole	**44**
2-cyano-tetrazole anion	**20**	5-nitramino-1H-tetrazole	**45**
5-cyano-tetrazole anion	**21**	5-nitramino-2H-tetrazole	**46**
1-hydroxyltetrazole	**22**	1-nitramino-tetrazole anion	**47**
2-hydroxyltetrazole	**23**	2-nitramino-tetrazole anion	**48**
5-hydroxyl-1H-tetrazole	**24**	5-nitramino-tetrazole anion	**49**
5-hydroxyl-2H-tetrazole	**25**		

Figure 1 illustrates the molecular structures of seven kinds of substituted tetrazole derivatives and their anions. All of the compounds studied in present paper are listed in Table 1. The hybrid DFT method based on Becke's 3-functional[42] with nonlocal correlation provided by the Lee,Yang, and Parr functional (LYP),[43] designated as B3LYP, is used throughout. All calculations were performed with GAUSSIAN92/DFT[44] program package. The optimized geometries obtained at the HF[45−47]/6-31G* level were adopted as the initial configurations. The optimizations were performed without any symmetry restrictions using the Fletcher−Powell[48] method and the default Gaussian convergence criteria. All of the optimized structures were characterized to be true relative energy minima of the potential surfaces by frequency calculations (no imaginary frequencies were found).

TABLE 2: Total Energies (E_T) and Heats of Formation (HOF) for the Reference Compounds[a]

compd	E_T	HOF	compd	E_T	HOF
1H-Tz	−258.25092	327.4	C_2H_6	−79.83043	84.68
2H-Tz	−258.25541	318.2	NH_2CN[b]	−148.76766	154.67
CH_4	−40.51840	−74.4	CH_3CN	−132.75494	75.32
$CH_3{-}NO_2$	−245.00933	−74.3	CH_3OH	−115.71439	−201.5
$NH_2{-}NO_2$	−261.03149	−3.2	CH_3Cl	−500.10854	−81.90
NH_3	−56.54794	−46.0	CH_3NH_2	−95.85320	−23.01
H^+	0.000000	1536.2	N_2H_4	−111.85386	95.40
NO_2Cl	−665.26128	12.13	HNO_2	−205.68693	−62.22
NH_2OH	−131.69581	−37.66			

[a] E_T: The total energies (Hartree). HOF: The heat of formation (kJ/mol). The data are from literature.[9,21,49,53−55] [b] The heat of formation for NH_2CN at 298.15 K in the gas phase is not available. We only find its heat of formation at 0 K (142.26 kJ/mol from ref 56). The value 154.67 kJ/mol in the table is the heat of formation at 0 K(142.26) plus 12.41. The latter is the change in enthalpy between 298.15 and 0 K which is calculated from the B3LYP/6-31G* calculation.

Our goal is to compute ΔH^{298} for each isodemic and isogyric reaction. It can be calculated using following expressions:

$$\Delta H^{298} = \Delta E^{298} + \Delta(PV) \quad (1)$$

$$\Delta E^{298} = \Delta E_e^0 + \Delta(\Delta E_e)^{298} + \Delta E_v^0 + \Delta(\Delta E_v^{298}) + \Delta E_r^{298} + \Delta \mathrm{E}_t^{298} \quad (2)$$

where each term in eq 1 and eq 2 is defined as follows: ΔE_e^0, energy difference between products and reactants at 0 K; $\Delta(\Delta E_e)^{298}$, change in the electronic energy difference between 0 and 298 K which is ignored in our calculations; ΔE_v^0, difference between the zero-point energies of the products and the reactants (at 0 K); $\Delta(\Delta E_v^{298})$, change in the vibrational energy difference between 0 and 298 K; ΔE_r^{298} and ΔE_t^{298}, changes in the rotational energy and the translational energy between products and reactants, respectively.

The $\Delta(PV)$ in eq 1 is the PV work term. It equals ΔnRT for reactions in the gas phase. For the isodemic reactions in the present paper, $\Delta n = 0$. For isogyric reactions, $\Delta n = 1$.

Table 2 contains the total energies and experimental HOFs for the reference compounds involved in this paper. As mentioned above, choosing reference compounds is a key point in setting up isodemic and isogyric reactions for obtaining high accuracy. In this paper, 1H and 2H-tetrazoles are used as reference compounds to avoid breaking down the delocalized bonds within the tetrazole skeleton ring.

As far as we know, there are two sets of experimental HOFs for 1H-tetrazole in the literature. One is 327.4 kJ/mol[21] and the other is 334.5 kJ/mol.[49] As all of the experimental HOFs of tetrazole derivatives cited here are from reference 21, to keep consistency we use the experimental HOF of 327.4 kJ/mol for 1H-tetrazole. For 2H-tetrazole, the HOF is 318.2 kJ/mol, which is the HOF of 1H-tetrazole minus the energy separation between 1H-tetrazole and 2H-tetrazole (9.2 kJ/mol).[27]

The designed isodemic and isogyric reactions for computing HOFs for the titled compounds were displayed in Table 3. Also listed in Table 3 is the calculated HOF of 2-methyl-5-ethenyltetrazole. For nitraminotetrazoles and hydrazinotetrazoles, the corresponding aminotetrazoles are used as the reference compounds because no experimental heats of formation for $NH_2{-}NH{-}NH_2$, $CH_3{-}NH{-}NH_2$, $NH_2{-}NH{-}NO_2$, and $CH_3{-}NH{-}NH_2$ are found. For the anions, the calculated HOFs of the corresponding neutrals are taken as the reference data. Both temperature correction (from 0 to 298.15 K) and zero-point vibrational energy correction are included in all calculations. The total energies (E_T) and calculated HOFs for all of the species investigated are listed in Table 3. One point should be pointed out that, unlike G-2 theory in which the zero-point vibrational energy is corrected by scaled frequencies at the HF/6-31G* level, the frequencies used for both temperature correction and zero-point vibrational energy correction in this paper are unscaled because our recent work[40] shows that the thermodynamic properties of 2H-tetrazole calculated with the unscaled frequencies at the B3LYP/6-31G* level agree satisfactorily with the experimental values. The largest absolute errors for H_m°, $C_{p,m}^\circ$ and S_m° between the calculated values and experimental results are 0.39 kJ/mol, 1.11 J K^{-1}/mol and 0.60 J K^{-1}/mol, respectively. Most recently A. A. El-Azhary and co-workers found that the agreement between the calculated (both scaled and unscaled) and experimental frequencies for tetrazole anion was excellent with the B3LYP method,[50] though a scaling factor (0.9613) for the B3LYP frequencies was suggested by M. W. Wong.[51] For the neutrals, the total energies and the temperature and zero-point vibrational energy correction for the reactants and products in the isodemic reactions are calculated at the B3LYP/6-31G* level, whereas for anions they are computed at the B3LYP/6-31+G* level. All computations were carried out on a Tontru Pentium personal computer in our laboratory.

Results and Discussions

Comparing the calculated HOFs (see Table 3) with the experimental ones for compounds **1**, **2**, **3**, **10,** and 2M-5ETz, one can see that they agree very well, except for compound **2**. The calculated error of HOF for **1**, **3**, **10,** and 2M-5ETz ranges from 0.11 kcal/mol to 2.29 kcal/mol. The average absolute deviation is 0.95 kcal/mol which is less than the average absolute deviation of 1.58 kcal/mol of the G-2 theory. The deviation is much smaller than the average absolute deviation of 3.11 kcal/mol derived from B3LYP calculated HOFs for 148 molecules.[19] This higher consistency is obviously due to the approach in which we adopt the tetrazole parent compounds (namely 1H-tetrazole and 2H-tetrazole) as the reference compounds. Our results seem to show that for calculating HOFs of series compounds, choosing the parent compounds as the reference compounds is a good idea for lowering calculation deviation. The large deviation (6.09 kcal/mol) with compound **2** is unknown. In our opinion, the heat of formation for **2** needs to be redetermined because experiments[1,52] indicate that 5-disubstituted 2H-tetrazoles are more stable than the corresponding 1H-isomers in the gas phase.

In the calculation of HOFs for 5-substituted tetrazolate anions we use two isogyric reactions. One is based on 5-substituted 1H-tetrazoles and the other on the 2H-isomers. From the calculated HOFs for compounds **7**, **14**, **21**, **28**, **35**, **42**, and **49**, we can see that HOFs predicted with different reactions are very close. The average deviation is 1.78 kcal/mol which is under the 2 kcal/mol target accuracy of the G-2 theory, indicating the consistency of the results from our B3LYP calculations is excellent.

From Table 3 one can see that HOFs of seven N1-substituted tetrazoles (**1**, **8**, **15**, **22**, **29**, **36**, and **43**) are consistently larger than the corresponding N2-substituted isomers. The difference of HOFs between the N1-substituted tetrazoles and the N2-substituted isomers lies between 0.68 and 8.89 kcal/mol. The average gap of heat of formation is 3.64 kcal/mol, which is close to the difference of HOFs (about 5 kcal/mol[21,52]) between 1,5-disubstituted tetrazoles and the corresponding 2,5-disubstituted isomers. It is also noted in Table 3 that apart from 5-nitramino-1H-tetrazole and 5-hydrazino-1H-tetrazole, all of

TABLE 3: Total Energies, Isodemic and Isogyric Reactions, and the Heats of Formation for the Titled Compounds

compd	E_T (Hartree)	Isodemic (Isogyric) reactions	HOF (kcal/mol)
2M-5ETz	−374.97866	2M-5ETz + CH_4 +NH_3 = 2H-Tz+$CH_3-CH=CH_2$+H_2N-CH_3	85.06 [84.61][a]
1	−297.56746 (−297.57994)[a]	1-methylTz + NH_3 = 1H-Tz + NH_2-CH_3	76.25 [77.21]
2	−297.57443 (−297.58713)	2-methylTz + NH_3 = 2H-Tz + NH_2-CH_3	72.43 [78.52]
3	−297.57590 (−297.58905)	5-methylTz(1H) + CH_4 = 1H-Tz + C_2H_6	67.01 [67.12]
4	−297.57918 (−297.59293)	5-methylTz(2H) + CH_4 = 2H-Tz + C_2H_6	65.50
5	−296.94738 (−296.98545)	1-methylTz = 1-methylTz anion + H^+	749.38
6	−296.92316 (−296.96306)	2-methylTz = 2-methylTz anion + H^+	766.52
7	−297.01994 (−297.05226)	5-methylTz(1H) = 5-methylTz anion + H^+	711.26
		5-methylTz(2H) = 5-methylTz anion + H^+	713.03
8	−313.57179 (−313.58697)	1-aminoTz + NH_3 = 1H-Tz + NH_2-NH_2	101.98
9	−313.57455 (−313.58989)	2-aminoTz + NH_3 = 2H-Tz + NH_2-NH_2	100.70
10	−313.60883 (−313.62530)	5-aminoTz(1H) + CH_4 = 1H-Tz + CH_3NH_2	75.13 [77.42]
11	−313.61398 (−313.63102)	5-aminoTz(2H) + CH_4 = 2H-Tz + CH_3NH_2	72.49
12	−312.95020 (−312.99149)	1-aminoTz	756.16
13	−312.92553 (−312.96874)	2-aminoTz = 2-aminoTz anion + H^+	771.48
14	−313.05168 (−313.08881)	5-aminoTz(1H) = 5-aminoTz anion + H^+	713.39
		5-aminoTz(2H) = 5-aminoTz anion + H^+	715.96
15	−350.46029 (−350.47378)	1-cyanoTz + NH_3 = 1H-Tz + NH_2-CN	131.77
16	−350.46218 (−350.47565)	2-cyanoTz + NH_3 = 2H-Tz + NH_2-CN	131.09
17	−350.48132 (−350.49596)	5-cyanoTz(1H) + CH_4 = 1H-Tz + CH_3-CN	118.16
18	−350.48712 (−350.50198)	5-cyanoTz(2H) + CH_4 = 2H-Tz + CH_3-CN	115.08
19	−349.88405 (−349.91895)	1-cyanoTz = 1-cyanoTz anion + H^+	737.83
20	−349.85875 (−349.89457)	2-cyanoTz = 2-cyanoTz anion + H^+	753.60
21	−349.96623 (−349.99777)	5-cyanoTz(1H) = 5-cyanoTz anion + H^+	699.53
		5-cyanoTz(2H) = 5-cyanoTz anion + H^+	702.20
22	−333.40528 (−333.36641)	1-hydroxylTz + NH_3 = 1H-Tz + NH_2-OH	75.39
23	−333.41174 (−333.37241)	2-hydroxylTz + NH_3 = 2H-Tz + NH_2-OH	71.94
24	−333.47117 (−333.43214)	5-hydroxylTz(1H) + CH_4 = 1H-Tz + CH_3-OH	31.97
25	−333.47398 (−333.43462)	5-hydroxylTz(2H) + CH_4 = 2H-Tz + CH_3-OH	30.78
26	−332.80038 (−332.84153)	1-hydroxylTz = 1-hydroxylTz anion + H^+	740.17
27	−332.77017 (−332.81352)	2-hydroxylTz = 2-hydroxylTz anion + H^+	760.24
28	−332.91882 (−332.95604)	5-hydroxylTz(1H) = 5-hydroxylTz anion + H^+	700.09
		5-hydroxylTz(2H) = 5-hydroxylTz anion + H^+	701.38
29	−368.87982 (−368.89943)	1-hydrazinoTz + NH_3 = 1-aminoTz + NH_2-NH_2	133.54
30	−368.89518 (−368.91378)	2-hydrazinoTz + NH_3 = 2-aminoTz + NH_2-NH_2	124.65
31	−368.92524 (−368.94508)	5-hydrazinoTz(1H) + NH_3 = 5-aminoTz(1H) + NH_2-NH_2	101.97
32	−368.92182 (−368.94213)	5-hydrazinoTz(2H) + NH_3 = 5-aminoTz(2H) + NH_2-NH_2	104.52
33	−368.27058 (−368.31525)	1-hydrazinoTz = 1-hydrazinoTz anion + H^+	756.96
34	−368.25671 (−368.30198)	2-hydrazinoTz = 2-hydrazinoTz anion + H^+	771.65
35	−368.35936 (−368.39946)	5-hydrazinoTz(1H) = 5-hydrazinoTz anion + H^+	725.21
		5-hydrazinoTz(2H) = 5-hydrazinoTz anion + H^+	723.79
36	−717.79488 (−717.80626)	1-chloroTz + HNO_2 = 1H-Tz + $Cl-NO_2$	114.74
37	−717.79937 (−717.81086)	2-chloroTz + HNO_2 = 2H-Tz + $Cl-NO_2$	112.39
38	−717.83808 (−717.85032)	5-chloroTz(1H) + CH_4 = 1H-Tz + CH_3Cl	77.37
39	−717.84346 (−717.85589)	5-chloroTz(2H) + CH_4 = 2H-Tz + CH_3Cl	74.52
40	−717.19910 (−717.23199)	1-chloroTz = 1-chloroTz anion + H^+	745.82
41	−717.17964 (−717.21122)	2-chloroTz = 2-chloroTz anion + H^+	760.43
42	−717.30617 (−717.33454)	5-chloroTz(1H) = 5-chloroTz anion + H^+	700.77
		5-chloroTz(2H) = 5-chloroTz anion + H^+	703.23
43	−518.03733 (−518.06101)	1-nitraminoTz + NH_3 = 1-aminoTz + NH_2-NO_2	122.13
44	−518.04644 (−518.07032)	2-nitraminoTz + NH_3 = 2-aminoTz + NH_2-NO_2	117.09
45	−518.08422 (−518.10805)	5-nitraminoTz(1H) + NH_3 = 5-aminoTz(1H) + NH_2-NO_2	89.75
46	−518.08340 (−518.10786)	5-nitraminoTz(2H) + NH_3 = 5-aminoTz(2H) + NH_2-NO_2	90.87
47	−517.45427 (−517.50181)	1-nitraminoTz = 1-nitraminoTz anion + H^+	738.55
48	−517.42866 (−517.47728)	2-nitraminoTz = 2-nitraminoTz anion + H^+	757.72
49	−517.55240 (−517.59554)	5-nitraminoTz(1H) = 5-nitraminoTz anion + H^+	701.74
		5-nitraminoTz(2H) = 5-nitraminoTz anion + H^+	701.47

[a] Values in the parentheses are total energies at B3LYP/6-31+G* level. Numbers in the square brackets are experimental data. Tz denotes tetrazole for neutrals or tetrazolate for anions, respectively.

the 5-substituted 1H-tetrazoles have larger HOFs than the corresponding 2H-isomers. The average difference in HOF is 2.25 kcal/mol. Structural analyses show that there are H-bonding interactions in 5-nitramino-1H-tetrazole, whereas the interaction does not exist in 5-nitramino-2H-tetrazole, which leads to the former having a lower HOF than the latter.[35] Our present results show that in the gas-phase most 5-substituted 2H-tetrazoles are more stable than the corresponding 1H-isomers.

From Table 3 it can also be noted that C-substituted tetrazoles are smaller in HOF than the corresponding N-substituted tetrazoles. The mean difference of HOF between C-substituted tetrazoles and N-substituted tetrazoles is 26.36 kcal/mol. From the molecular structure (see Figure 1) we can see that the HOF difference between C-substituted and N-substituted tetrazoles mainly results from the difference of bond energy between R−C and R−N. Here R refers to the atom attached to the tetrazole ring (i.e., O atom in hydroxyltetrazoles, N atom in aminotetrazoles, hydrazinotetrazoles and nitraminotetrazoles, C atom in methyltetrazoles and cynaotetrazoles, and Cl atom in chlorotetrazoles). As the bond energy for R−C is larger than that for R−N, therefore the C-substituted tetrazoles have lower heats of formation than the corresponding N-substituted isomers. The calculated HOF difference between C-substituted tetrazoles and the N-substituted isomers is in good agreement with the corresponding bond energy gap, indicating that the calculated heats of formation are reasonable. For example, bond energy for O−C is greater than that for O−N by 41.83 kcal/mol,[57] while the difference in HOF between C-substituted hydroxyltetrazoles (**24** and **25**) and the N-substituted hydroxyltetrazoles (**22** and **23**) is 42.29 kcal/mol on average. The fact that C-substituted tetrazoles are more stable than the N-substituted isomers may account for the phenomenon that so far most work on tetrazoles is focused on the C-substituted tetrazoles.

For twenty one tetrazolate anions, all of the C-substituted ions have the lowest HOFs. The HOF gap between C-substituted tetrazolate ions and the N-substituted ones are larger than that of the neutrals. It is worth noting that although 2-substituted tetrazoles are more stable than the 1-substituted isomers, the corresponding 1-substituted tetrazolate anions are lower in HOF than those of 2-substituted isomers. According to the calculated HOFs for the three kinds of tetrazolate ions, the order of stability is as follows: C-substituted tetrazolate ions > N1-substituted ones > N2-substituted tetrazolate anions, which is consistent with the fact that most metal complexes of tetrazole are formed with C-substituted tetrazolate anions.

Conclusions

Our calculations of HOFs for 49 tetrazole derivatives show that the DFT-B3LYP method can produce accurately and economically the HOFs for tetrazole compounds. Keeping delocalized bonds in setting up isodemic reactions is a good way for calculating HOF for compounds containing the delocalized bonds. Our results indicate that C-substituted tetrazoles and 2H-tetrazoles are more stable than the corresponding N-substituted isomers and 1H-tetrazole isomers, respectively. Finally, there is a substantial discrepancy between the theoretical value (72.43 kcal) and the experimental result (78.52 kcal/mol) of 2-methyltetrazole. The good agreement between the remaining theoretical and experimental heats of formation suggests that further experimental investigation of 2-methyltetrazole is called for.

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