Application of Mass Spectrometry to the Study of Prototropic Equilibria in 5-Substituted Tetrazoles in the Gas Phase; Experimental Evidence and Theoretical Considerations

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The tautomerism of tetrazole, 5-methyltetrazole, and its isotopically substituted derivatives is discussed on the basis of their fragmentation patterns, and of quantum chemical calculations by the LCAO MO method in the CNDO/2 approximation. The equilibrium of these compounds in the gas phase is displaced towards the 2*H*-tautomer. Analysis of the mass spectra of 5-methyl[$^2H_3$]tetrazole revealed randomization of hydrogen between the methyl and the NH groups.

Our studies on the correlational analysis of a group of 'tetrazolic acids' (5-substituted tetrazoles),[1-4] involved the use of mass spectrometry. Reports on mass spectrometric investigations of tetrazoles are scarce.[5-14] They have been mostly confined to di- and tri-substituted compounds which display specific fragmentation patterns. Fragmentation patterns of 5-substituted tetrazoles have been described by Forkey and Carpenter [8] (tetrazole and its 5-methyl-, 5-trideuteriomethyl-, and 5-trifluoromethyl-derivatives) and by Brady [10] (5-aminotetrazole). We have extended these investigations to include the fragmentation of the tetrazole ring in 5-substituted tetrazoles, and have also revised some of the earlier reported results. Another reason for our interest in the method was the possibility of utilizing it to investigate prototropic equilibria, including those of 5-substituted tetrazoles, in the gas phase.

Previous, investigations of the tautomeric equilibria of 5-substituted tetrazoles (1) ⇌ (2) have been faced with considerable difficulties, and the results reported hitherto for equilibria in solution are often conflicting.[15]

We have now studied tetrazole (1a), 5-methyltetrazole (1b), and its isotopically substituted analogues 5-methyl[1- or 4-^{15}N]tetrazole (1c) and 5-methyl[$^2H_3$]tetrazole (1d). The mass spectrometric results were compared with those of semi-empirical (CNDO/2) quantum chemical calculations for tetrazole and 5-methyltetrazole.

Methods

Mass Spectra.—Mass spectra were recorded on a high-resolution Varian MAT-711 double-focusing spectrometer with Mattauch-Herzog geometry at 1 000 resolution. Samples were introduced at a probe temperature of 50 °C. The spectra were recorded at ion accelerating voltage 8 kV, ionization energy 70 eV, and electron trap current 800 μA using a galvanometric u.v. recorder. High-resolution measurements were performed for $R = 10\,000$ using a peak matching technique and PFK (high boiling perfluorokerosine; Merck), nitrogen, and acetone as the standards. The spectra of metastable ions were recorded by a defocusing technique; the accelerating voltage was scanned from 2 kV and the values of the focusing voltage read from a digital voltmeter with accuracy ±1 V.

Tetrazole (1a) was a commercial product (Fluka). 5-Methyltetrazole (1b) was previously synthesized.[16] 5-*Methyl*[1- *or* 4-^{15}N]*tetrazole* (1c) [m.p. 145—146 °C (Found: C, 29.55; H, 2.9; N, 67.4. $C_2H_4N_3{}^{15}N$ requires C, 29.4; H, 2.75; N, 67.85%)] was synthesized from $CH_3C^{15}N$ (Berlin-Chemie) by the method described previously.[16] Similarly, 5-*methyl*[$^2H_3$]-*tetrazole* (1d) was obtained from CD_3CN [m.p. 148 °C (Found: C, 27.45; H, 7.95; N, 64.0. $C_2HD_3N_4$ requires C, 27.6; H, 8.05; N, 64.45%)].

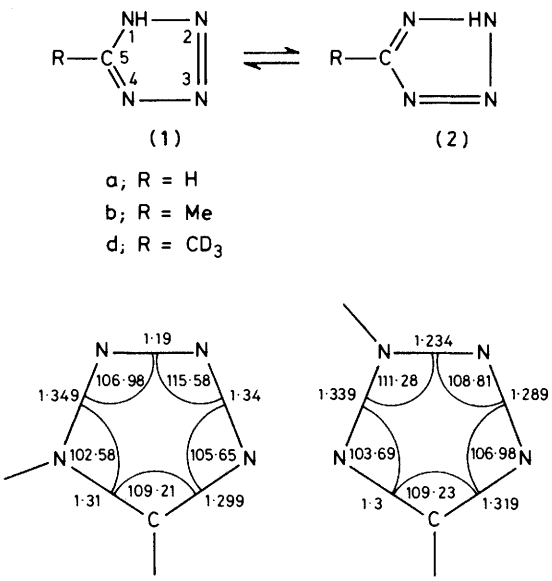


Figure 1. Geometry of tautomeric forms of tetrazole

Theoretical Calculations.—Theoretical calculations were performed by the quantum chemical LCAO MO method in the CNDO/2 approximation, with Pople's original parametrization.[17,18] In the calculations, the geometry of the tetrazole ring (Figure 1) was assumed on the basis of *X*-ray structural data for 5-methyltetrazole derivatives.[19] The geometry was modified in such a manner as to achieve agreement between the dipole moments of both tautomeric forms calculated by us and tabulated by McClellan.[20]

In the CNDO/2 method, the total energy can be represented as the sum of the mono- and bi-centre terms: [21]

$$E_{total} = \sum_{\alpha} E_{\alpha} + \sum_{\alpha<\beta}\sum E_{\alpha\beta}$$

where $E_{\alpha} = \sum_{\mu_\alpha} P_{\mu_\alpha\mu_\alpha}\mu_{\mu_\alpha\mu_\alpha} + 1/2\sum_{\mu_\alpha}\sum_{\gamma_\alpha}(P_{\mu_\alpha\mu_\alpha}P_{\gamma_\alpha\gamma_\alpha} - 1/2P^2{}_{\mu_\alpha\gamma_\alpha})_{\gamma_\alpha\alpha}$

Table 1. Partial mass spectra of tetrazole (1a), 5-methyltetrazole (1b), and 5-methyl[$^2H_3$]tetrazole (1d)

Tetrazole		5-Methyltetrazole		5-Methyl-[$^2H_3$]tetrazole	
m/z	%	*m/z*	%	*m/z*	%
27	33	27	62	26	11
28	>100	28	>100	27	20
29	27	29	47	28	>100
41	17	30	4	29	54
42	100	38	8	30	68
43	22	39	12	31	14
70	34	40	30	32	12
		41	43	40	16
		42	17	41	6
		43	11	42	28
		55	25	43	26
		56	100	44	45
		57	4	45	25
		84	11	57	39
				58	19
				59	100
				87	31

$P_{\mu_\alpha\mu_\alpha}$ is the electron density on orbital μ

$$E_{\alpha\beta} = E_{\alpha\beta}^{(1)} + E_{\alpha\beta}^{(2)} + E_{\alpha\beta}^{(3)}$$

$$E_{\alpha\beta}^{(1)} = 2\sum_{\mu_\alpha}\sum_{\gamma_\beta} P_{\mu_\alpha\gamma_\beta}\delta_{\mu_\alpha\gamma_\beta}\beta'_{\alpha\beta}$$

$$E_{\alpha\beta}^{(2)} = 1/2\sum_{\mu_\alpha}\sum_{\beta_\gamma} P^2_{\mu_\alpha\gamma_\beta}\gamma_{\alpha\beta}$$

$$E_{\alpha\beta}^{(3)} = P_{\alpha\alpha}P_{\beta\beta}\gamma_{\alpha\beta} - P_{\alpha\alpha}Z_\beta\gamma_{\alpha\beta} - P_{\beta\beta}Z_\alpha\gamma_{\alpha\beta} + Z'_\alpha Z'_\beta R_{\alpha\beta}^{-1}$$

$P_{\alpha\alpha}$ is the total electron density on an atom

$\delta_{\mu_\alpha\gamma_\beta}$ is the integral of the orbital overlap

$\mu_{\mu_\alpha\mu_\beta}$, $\gamma_{\alpha\alpha}$, $\beta_{\alpha\alpha}$, Z'_α are empirical parameters of the CNDO/2 method.

The bicentre terms are of paramount importance for the description of bond energies. For instance, the $E_{\alpha\beta}^{(1)}$ term is a measure of the contribution of orbitals α and β (both bonding and antibonding), a negative value denoting the bonding character. The $E_{\alpha\beta}^{(2)}$ term is always negative and represents stabilization of the α–β pair by exchange effects. The $E_{\alpha\beta}^{(3)}$ term accounts for electrostatic interaction of the two atoms considered.

Results and Discussion

Mass Spectra.—The spectra of tetrazole (1a), 5-methyltetrazole (1b), and 5-methyl[$^2H_3$]tetrazole (1d) resemble those reported by Forkey and Carpenter.[8] Specific ions are listed in Table 1.

To elucidate the fragmentation pathways, we also synthesized 5-methyl[1- or 4-^{15}N-]tetrazole. Its spectrum is shown in Figure 2.

A characteristic feature of all the spectra is the presence of relatively abundant molecular ions [*m/z* 70, 84, 85, and 87 for (1a—d), respectively], which enabled isotopic homogeneity to be determined. In no case was the presence of ions formed by abstraction of H· observed. In accord with Forkey and Carpenter's findings, the most abundant ions correspond to the loss of N_2 from the molecular ion. The use of the ^{15}N-labelled 5-methyltetrazole enabled the mode of elimination of N_2 from the tetrazole ring to be traced.

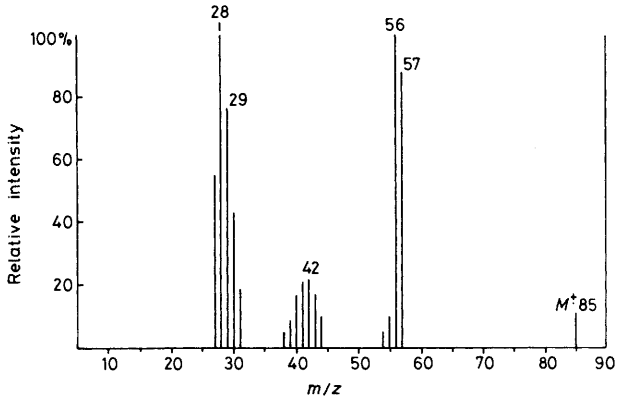
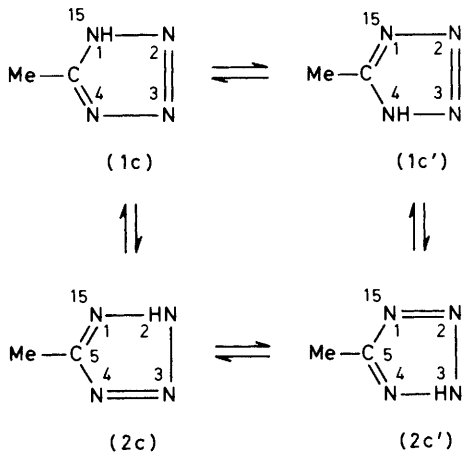


Figure 2. Mass spectrum of 5-methyl[1- or 4-^{15}N]tetrazole

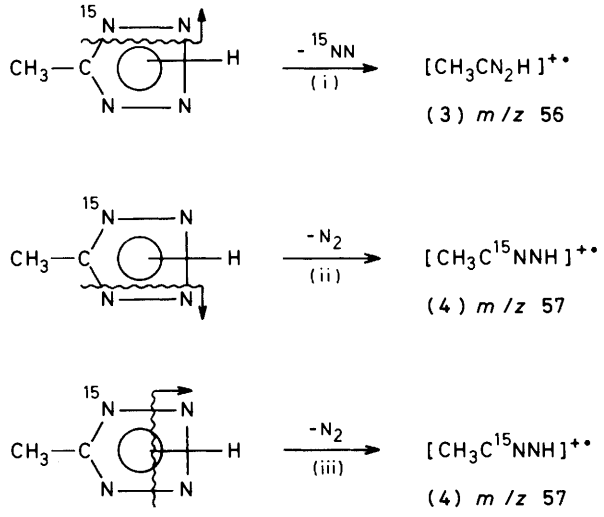


Scheme 1

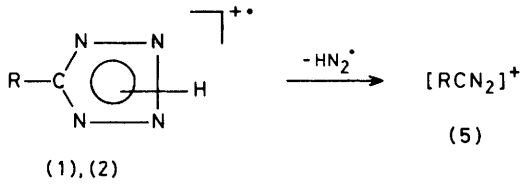
Compound (1c) can occur in the tautomeric forms shown in Scheme 1. Considerations of bond multiplicity imply that in tautomers (1c) and (1c') nitrogen elimination should arise from preferential cleavage of the N(1)–N(2) and N(3)–N(4) bonds, whilst with tautomers (2c) and (2c'), the N(2)–N(3) and N(4)–C(5) bonds should be broken. The elimination of N_2 can be realized by three pathways (Scheme 2). The ratio of abundances of the ions at *m/z* 56 [pathway (i)] and 57 [pathways (ii) and (iii)], if one assumes equal probabilities for the three pathways, should be 1 : 2. Experiment showed this ratio to be 1 : 1.3. Hence, since pathways (i) and (ii) *are* equally probable, pathway (iii) is considerably less likely. This finding may indicate the displacement of the tautomeric equilibrium in 5-methyltetrazole in the gas phase towards the 2*H*-tautomer [tautomers (2c) and (2c')].

With compound (1c) we detected two ions at *m/z* 56, of composition $[CH_3C^{15}NN]^+$ (arising by ejection of $N_2H^\cdot$ from the molecular ion) and $[CH_3CN_2H]^{+\cdot}$. Their relative contributions to the peak, as estimated from high-resolution measurements, amounted to 1 : 2.

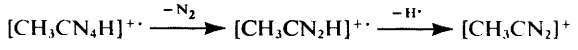
The second mode of decay of the molecular ions of tetrazole, 5-methyltetrazole, and its labelled derivatives consists of elimination of the $HN_2^\cdot$ radical (Scheme 3). With (1c), either $HN_2^\cdot$ or $H^{15}NN^\cdot$ may be ejected, thus producing two ions,



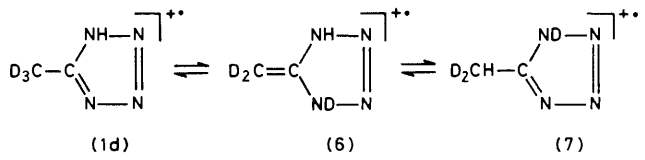
Scheme 2.



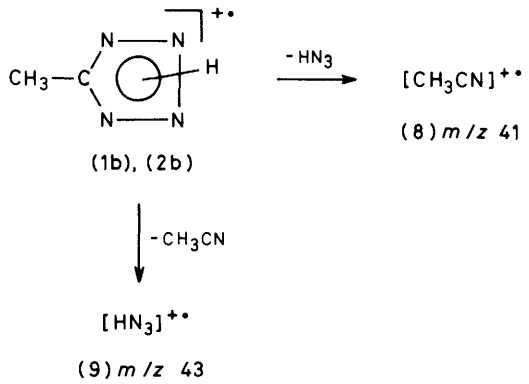
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

m/*z* 56 and 55, having the compositions $[CH_3C^{15}NN]^+$ and $[CH_3CN_2]^+$, respectively. The 56 : 55 intensity ratio, determined from high-resolution measurements, was 3.7 : 1. As the mechanism of this fragmentation has not been elucidated, no conclusion as to tautomeric preference can be drawn from this finding.

A comparison of isotopic ratios of the ions from the ^{15}N counterpart of 5-methyltetrazole revealed the formation of the $[M - HN_2]$ ion *via* a two-stage fragmentation (Scheme 4) to be of little significance, although the two possibilities were taken into account by Forkey and Carpenter.[8] For 5-trideuteriomethyltetrazole (1d) they suggested elimination of the methyl hydrogen atom during loss of the $HN_2^{\cdot}$ radical. We suggest an entirely different interpretation of the experimental evidence based on total randomization of the hydrogen atoms within the molecular ion of 5-methyltetrazole. On the assumption of such randomization, the probability of finding deuterium or protium in the NH(D) group amounts to 3 : 1. The experimentally determined abundance ratio of the *m*/*z* 58 to *m*/*z* 57 ions arising from elimination of $HN_2^{\cdot}$ and $DN_2^{\cdot}$ respectively, is 1 : 3, thus confirming full randomization of hydrogen or deuterium. A preference for elimination of $DN_2^{\cdot}$ or $HN_2^{\cdot}$ is thus of little importance for elucidation of the fragmentation pattern. The full randomization of the hydrogen or deuterium atoms can be rationalized in terms of the processes shown in Scheme 5 taking place after ionization.

The mass spectra of compounds (1a—d) display peaks at *m*/*z* 29 $[HN_2]^+$. With (1c), a peak at *m*/*z* 30 $[H^{15}NN]^+$ is also observed. If these ions were generated from the molecular ion, their intensity ratio for (1c) should be the reciprocal of that of *m*/*z* 55 $[CH_3CN_2]^+$ and *m*/*z* 56 $[CH_3C^{15}NN]^+$. However, the experimentally found ratio for *m*/*z* 29 and 30 is 2 : 1. However, the $[HN_2]^+$ ion can also arise from the $[HN_3]^+$ ion (*m*/*z* 43), which is formed by still another fragmentation of the molecular ion (Scheme 6). The empirical intensity ratio of the $[CH_3CN]^{+\cdot}$ (*m*/*z* 41) and $[CH_3C^{15}N]^{+\cdot}$ (*m*/*z* 42) ions, established from high-resolution measurements for compound (1c), is 1 : 1, in agreement with expectations. This fragmentation pattern of the molecular ion of 5-methyltetrazole to produce the acetonitrile and hydrazoate ions, established on the basis of a thorough mass spectrometric analysis of compound (1c), appears to be incontrovertible, and characteristic of 5-substituted tetrazoles. This decay is a reversal of the common synthetic pathway leading to 5-substituted tetrazoles, by cycloaddition of nitriles to hydrazoic acid.[22,23] The acetonitrile ions appearing in the spectrum of 5-trideuteriomethyltetrazole (1d) are characterized by *m*/*z* ratios of 43 and 44 and respective compositions $[CD_2HCN]^{+\cdot}$ and $[CD_3CN]^{+\cdot}$, their relative abundances correspond to statistical distribution of hydrogen atoms, thus confirming full randomization.

Quantum Chemical Calculations.—The primary objective of the theoretical calculations was to obtain data helpful in interpreting the mass spectrometric results. First it was of interest to learn which of the tautomers (1) or (2) would theoretically be more liable to ionization and fragmentation, and in particular which of the bonds in the tetrazole ring would be expected to undergo preferential cleavage.

Theoretical calculations for tetrazole [24-30] and its 5-amino-derivative [31] had been performed earlier by various methods. However, these papers were mostly concerned with the geometry of the tetrazole ring and pertinent calculations of the dipole moments of the tautomeric forms.[25-27,30,31] The ionization energy values calculated in some instances [24,25] were obtained by accounting for π-orbitals only. To the best of our knowledge, there is no report dealing with bond energies in the tetrazole molecule and its radical.

On the basis of the assumed geometry of the tetrazole ring, we estimated total energies for both tetrazole tautomers and for 5-methyltetrazole (Table 2).

Table 2. Total energy and ionization energy of tautomers of tetrazole and 5-methyltetrazole

Compound	Un-ionized form		Ionized form		Ionization energy	
	Total energy (a.u.)	Dipole moment (D)	Total energy (a.u.)	Dipole moment (D)	$I = \Delta E$ (eV)	$I = -E_i$ (eV)
Tetrazole						
1*H*-tautomer	−55.286	5.167	−54.836	4.759	12.278	13.488
2*H*-tautomer	−55.297	2.344	−54.845	5.743	12.213	13.226
5-Methyltetrazole						
1*H*-tautomer	−63.986	5.458	−63.555	3.841	11.696	12.671
2*H*-tautomer	−63.996	2.111	−63.566	4.389	11.708	12.699

Table 3. Bond energies (a.u.)

Bond	1*H*-Tautomer				2*H*-Tautomer			
	$E_{\alpha\beta}^{(1)}$	$E_{\alpha\beta}^{(2)}$	$E_{\alpha\beta}^{(3)}$	$E_{\alpha\beta}^{total}$	$E_{\alpha\beta}^{(1)}$	$E_{\alpha\beta}^{(2)}$	$E_{\alpha\beta}^{(3)}$	$E_{\alpha\beta}^{total}$
Un-ionized tetrazole								
N(1)–N(2)	−1.184	−0.206	−8.871	−10.233	−1.227	−0.180	−8.913	−10.319
N(2)–N(3)	−1.734	−0.368	−9.778	−11.880	+0.014	−0.005	−5.751	−5.743
N(3)–N(4)	−1.225	−0.222	−8.901	−10.347	−1.317	−0.284	−9.184	−10.784
N(4)–C(5)	−1.572	−0.294	−7.157	−9.022	−0.072	−0.003	−4.682	−4.702
C(5)–N(1)	−1.455	−0.264	−7.067	−8.768	−0.035	−0.029	−4.727	−4.791
Ionized tetrazole								
N(1)–N(2)	−1.233	−0.217	−8.846	−10.296	−1.220	−0.216	−8.909	−10.344
N(2)–N(3)	−1.750	−0.240	−9.761	−11.752	−0.007	−0.029	−5.751	−5.794
N(3)–N(4)	−1.196	−0.203	−8.905	−10.305	−1.404	−0.263	−9.176	−10.844
N(4)–C(5)	−1.560	−0.306	−7.149	−9.015	−0.022	−0.005	−4.675	−4.702
C(5)–N(1)	−1.421	−0.244	−7.063	−8.728	−0.016	−0.008	−4.723	−4.747
Un-ionized 5-methyltetrazole								
N(1)–N(2)	−1.169	−0.203	−8.845	−10.217	−0.958	−0.218	−8.914	−10.090
N(2)–N(3)	−1.727	−0.370	−9.778	−11.875	+0.012	−0.030	−5.749	−5.765
N(3)–N(4)	−1.220	−0.224	−8.900	−10.344	−1.411	−0.285	−9.184	−10.879
N(4)–C(5)	−1.532	−0.300	−7.163	−8.995	−1.760	−0.002	−4.682	−4.701
C(5)–N(1)	−1.415	−0.227	−7.070	−8.712	+0.035	−0.011	−4.726	−4.702
C(5)–C(6)	−1.308	−0.192	−5.298	−6.798	−1.307	−0.191	−5.297	−6.794
Ionized 5-methyltetrazole								
N(1)–N(2)	−1.224	−0.212	−8.848	−10.284	−1.209	−0.200	−8.912	−10.312
N(2)–N(3)	−1.754	−0.309	−9.764	−11.827	−0.009	−0.009	−5.760	−5.778
N(3)–N(4)	−1.194	−0.202	−9.005	−10.401	−1.200	−0.239	−9.180	−10.617
N(4)–C(5)	−1.519	−0.286	−7.157	−8.926	−0.001	−0.004	−4.672	−4.676
C(5)–N(1)	−1.393	−0.216	−7.067	−8.676	−0.015	−0.003	−4.720	−4.738
C(5)–C(6)	−1.314	−0.193	−5.302	−6.809	−1.318	−0.195	−5.302	−6.815

The values of the ionization energies listed in Table 2 were calculated in two ways: (i) from Koopman's theorem [32] ($I_i = -E_i$; *i.e.* the ionization energy is equal to the energy of the highest occupied orbital in a molecule); (ii) from the difference between total energies of the unionized and ionized molecules. The latter approach afforded lower values of the ionization energy than the former. As the CNDO/2 method affords I_i values too high in comparison with the empirical ones, the latter method seems more suitable, particularly as it accounts for variations in electron distribution after ionization. The experimental ionization energy for tetrazole (*ca.* 11.4 eV) has been found from the photoelectron spectrum.[30]

The calculated total energy values suggest that the forms (2) (2*H*-tautomer) of tetrazole and 5-methyltetrazole are energetically favoured in the gas phase. The differences in energy between the tautomeric forms of the two compounds are 6.528 (0.283 eV) and 6.805 kcal mol^{-1} (0.295 eV), respectively. The values of the dipole moments and their changes upon ionization are also shown in Table 2. The high values of the dipole moments of tautomers (1) of tetrazole and 5-methyltetrazole are in good agreement with the known empirical value (5.25 D) [20] determined for tetrazole in dioxan. Most authors conclude from experimental evidence that tetrazole occurs in form (1) in solution on account of its better solvation.

Upon ionization in the mass spectrometer, the dipole moment of a molecule should increase. Data listed in Table 2 show that tautomers (2) of tetrazole and 5-methyltetrazole, after conversion into radical ions, display higher dipole moments values than the un-ionized molecules. On the other hand, the dipole moments of the ionized forms of tautomers (1) are lower than those of the un-ionized molecules. Krugh and Gold [33] have studied the tautomerism of tetrazole in gas phase in relation to dipole moments. By using microwave spectra for the determination of the dipole moments of tetrazole and its *C*- and *N*-deuteriated derivatives, they found tetrazole and *N*-deuteriotetrazole to occur in the gas phase predominantly as the 2*H*-tautomers, while for *C*-deuteriotetrazole they claimed that the tautomeric equilibrium was displaced towards the 1*H*-tautomer.[33]

We calculated the $E_{\alpha\beta}$ values for the un-ionized and ionized tautomeric forms of tetrazole and 5-methyltetrazole (Table 3). With both compounds, the calculated values of the bicentre terms are much higher for tautomers (2) than for (1). From considerations of the stability of the molecule from this standpoint, it can be concluded that tautomers (2) are more prone to fragmentation in the mass spectrometer than tautomers (1). An analysis of the numerical values of the total bicentre energy, $E_{\alpha\beta}$, of tautomer (2) show that the C(5)–N(4)

C(5)–N(1) and N(2)–N(3) bonds should be the most readily broken. This should result in elimination of either a nitrogen molecule or with a slightly lower probability of the $NH_2^{\bullet}$ radical. A further factor supporting this fragmentation sequence is represented by the $E_{\alpha\beta}^{(1)}$ values for tautomers (2) With 5-methyltetrazole, $E_{45}^{(1)}$ assumes a positive value after ionization, thus revealing the antibonding nature of the association of this pair of atoms (Table 3). The next most weakly associated pair of atoms in the radical ion is C(5)–N(1), followed by N(2)–N(3). These findings are in agreement with the mass spectrometric results. If 5-methyltetrazole occurred in the mass spectrometer as tautomer (1), the $E_{\alpha\beta}$ values calculated for particular pairs of atoms would suggest breaking of the C(5)–C(6) bond, thus giving rise to a peak at m/z $[M - 15]^+$ (loss of $CH_3^{\bullet}$). However, the $[M - CH_3]^+$ peak is missing from the spectra of 5-methyltetrazole and its isotopic analogues.

In our opinion, both the mass spectrometric results and the theoretical calculations demonstrate explicitly the occurrence of tautomers (2) (2*H*-tautomers) of tetrazole and 5-methyltetrazole in the gas phase. It should be borne in mind that isomeric equilibria of ionic species do not necessarily reflect those of neutral systems. However, because of the involvement of electron impact, most probably the results reveal the preferential isomeric distribution before ionization in such a system as the tetrazole ring.

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