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International Journal of Mass Spectrometry 185/186/187 (1999) 925–933



Pyrazine diradicals, carbenes, ylides, and distonic ions probed by theory and experiment

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Received 31 August 1998; accepted 18 September 1998

Abstract

The [C₄H₄N₂] potential energy hypersurface relating to pyrazine and its hydrogen shift isomers has been investigated computationally using hybrid Hartree–Fock/density functional theory and through a variety of tandem mass spectrometry experiments (metastable ion, collision-induced dissociation, and neutralization reionization mass spectrometry). In addition to the conventional pyrazine structure **1**, its α -ylide **2**, β -ylide **3**, and the 1,4-diradical **4** were generated and characterized through neutralization reionization mass spectrometry experiments. Also, the corresponding radical cations **1**^{+•}–**4**^{+•} were accessible by dissociative electron ionization of the appropriate pyrazine esters. Quantum chemical calculations at the B3LYP/TZVP level of theory reveal that all these species correspond to minima that are separated by significant barriers thus preventing facile isomerization. As an additional, albeit high lying isomer, the 1,3-diradical **5** was computationally identified. In the case of the radical cations the energy differences between the various isomers are much smaller than for the corresponding neutrals; however, pyrazine represents in both cases the most stable species. (Int J Mass Spectrom 185/186/187 (1999) 925–933) © 1999 Elsevier Science B.V.

Keywords: Carbenes; Neutralization/reionization; Ylides; Distonic ions; Density functional calculations

1. Introduction

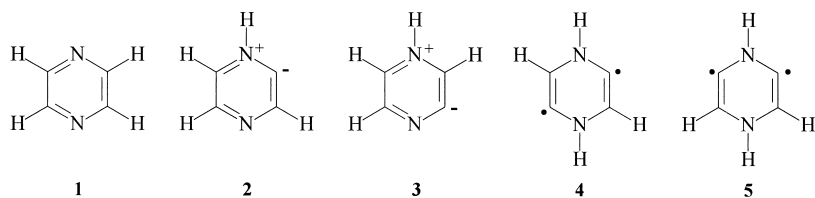
There seems a near ubiquitous interest of chemists in nitrogen heterocycles. The biochemical importance of such species diminishes in no way the fascination

of physical and organic chemists in understanding and probing their intrinsic structures, properties, and dynamics [1,2]. In the latter context, desmotropy [3], the process of isolating individual tautomers or isomers, is an ever popular endeavor. The molecules most sought after in this respect are often those that represent classes of reactive intermediates, such as the carbene or ylide isomers of the imidazoles [4] that were eventually obtained as isolable substances by Arduengo and co-workers [5]. Sometimes, as is the case for the parent imidazolylidene (C₃H₄N₂) [6,7], the gas phase is the refuge of certain fugitive hetero-

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Dedicated to Professor M.T. Bowers on the occasion of his 60th birthday.



Scheme 1. $[C_4H_4N_2]$ species considered: pyrazine **1**, the α -ylide **2**, the β -ylide **3**, the 1,4-diradical **4**, and the 1,3-diradical **5**.

cyclic intermediates. The related thiazolyliene (C_3H_3NS) [8] and pyridinylidene (C_5H_5N) [7,9] are only a couple of many interesting species generated and characterized in the gas phase via the technique of neutralization reionization mass spectrometry (NRMS) [10,11]. Nevertheless, many other species exist only as “virtual molecules”: viable according to sophisticated quantum chemical computations but experimentally unobserved.

The present work focuses on identifying molecules and radical cations in the $[C_4H_4N_2]$ six-member ring system relating to pyrazine and its hydrogen-shift isomers. To this end we used a combined experimental/computational approach relying on hybrid Hartree–Fock/density functional theory and a variety of tandem mass spectrometry experiments (metastable ion, collision-induced dissociation, and neutralization reionization mass spectrometry). Attention was directed particularly toward the neutral isomers of pyrazine **1** that are shown in Scheme 1: the α -ylide **2**, the β -ylide **3**, the 1,4-diradical **4**, and the 1,3-diradical **5**.

Stationary points corresponding to neutral molecules **1–5** in the lowest singlet and triplet states, the corresponding doublet states of the radical cations [12], and the transition structures for their interconversions via 1,2-hydrogen shifts were located at the B3LYP/TZVP level of theory. In addition to **1**, three of the viable isomers **2–4** were experimentally generated through one-electron reduction of their radical cations in NRMS experiments [10,11]. Structural characterization of ions and of neutrals in this system is not facile and it proved advantageous to perform, specifically on the ions that survived the neutralization reionization process, collision-induced dissociation

experiments. These are denoted as NR/CID experiments [11].

2. Theoretical details

The calculations of the structures, energies, and frequencies were performed on IBM/RS6000 workstations and a CRAY Y-MP using the GAUSSIAN 94 program package [13]. The accuracy of the hybrid density functional approach in this regard was previously demonstrated for pyridine and its ylide by comparison of B3LYP with complete active space SCF (CASSCF) and highly correlated coupled cluster [CCSD(T)] type calculations [9,14]. In all cases, the CCSD(T) and B3LYP results were in very good agreement. Calculations for selected species of the present context employing the CCSD(T) method confirmed this conclusion. We therefore decided to use the B3LYP hybrid density functional theory option employing Becke’s [15] empirical three-parameter fit for mixing HF and DFT exchange–energy terms as implemented [16] in GAUSSIAN 94 for the present study on the neutral and ionic $[C_4H_4N_2]$ species. All the neutral species and their respective radical cations are identified as genuine minima characterized by a positive definite Hessian matrix. Initial geometry optimizations were performed with the standard 6-31G** basis set [17]. Subsequently, Ahlrichs’ polarized TZVP basis set [18] was used to improve the quality of the results. All data given in the following correspond to B3LYP/TZVP geometries and energies corrected for zero-point vibrational energy (ZPE) contributions [19]. No scaling of the ZPE was performed for the B3LYP fundamentals. For the open shell

Table 1

Total [E_h] and relative [E_{rel} , kcal mol⁻¹] energies for species discussed in the text as computed at B3LYP/TZVP. Relative energies are corrected for zero point vibrational energies (ZPE)

Species	Singlet	ZPE	E_{rel}	Triplet	ZPE	E_{rel}	Species	Doublet	ZPE	E_{rel}
1	-264.4031	48.0	0.0	-264.2835	43.7	70.8	1⁺	-264.0668	46.1	0.0
2	-264.3311	48.0	45.2	-264.2814	45.9	74.3	2⁺	-264.0499	48.1	12.7
3	-264.2973	46.6	65.0	-264.2917	46.0	67.9	3⁺	-264.0601	48.4	6.6
4	-264.2693	47.5	83.5	-264.2320	45.5	104.9	4⁺	-263.9851	47.5	52.7
5	-264.2602	47.9	89.6	-264.2366	46.0	102.6	5⁺	-263.9916	47.9	49.1
TS1/2	-264.2589	43.6	86.0	-264.1916	41.7	126.3	TS1^{·+}/2^{·+}	-263.9561	43.0	66.4
TS2/3	-264.2031	43.1	120.6	-264.1883	42.4	129.2	TS2^{·+}/3^{·+}	-263.9298	43.8	83.7
TS3/5	-264.1699	42.9	141.2	-264.1544	41.9	149.9	TS3^{·+}/5^{·+}	-263.9077	43.5	97.3
TS4/5	-264.1619	43.0	146.3	-264.1480	42.6	154.4	TS4^{·+}/5^{·+}	-263.8793	43.1	114.7
TS2/4	-264.1923	43.3	127.6	-264.1585	41.8	147.3	TS2^{·+}/4^{·+}	-263.9132	43.5	93.9

species the unrestricted Kohn–Sham scheme was employed. The $\langle S^2 \rangle$ expectation value of the noninteracting Kohn–Sham determinant was in all cases very close to the exact values [20].

3. Experimental procedure

The mass spectrometric experiments were performed at McMaster University on the VG Analytical ZAB-R. The details of this instrument and also for the acquisition of neutralization reionization (NR) mass spectra have been previously described [21]. Briefly, the NR experiments were performed on mass-selected ions between the magnet (B) and the first electric sector (E_1) of the BE₁E₂ geometry ZAB-R. There are two small gas cells in this region: the first pressurized with *N,N*-dimethylaniline vapor that neutralizes a small fraction of the 10 kV source generated ions by electron transfer and the second containing oxygen that reionizes some of the high speed neutrals via collisions. In between the cells is a positively charged deflector to ensure that only neutrals enter the second cell. The mass spectra are recorded with a PC-based data system (Mommers Technologies Inc., Ottawa, Canada) by scanning E_1 . Collision-induced dissociation (CID) mass spectra were obtained in the same region with the first cell empty and the deflector switched off. The NR/CID (see text) and CID mass spectra were obtained by scanning E_2 , with E_1 set at a fixed potential and with oxygen as the collision gas in another small cell located between E_1 and E_2 .

Pyrazine was used as purchased (Aldrich Chemical Co., St. Louis). Methyl-2-pyrazinecarboxylate and dimethyl-2,3-pyrazinedicarboxylate, the precursor molecules for **2⁺** and **3⁺**, were synthesized by esterification of their readily available mono and dicarboxylic acids. The precursor molecule for generating **4⁺**, dimethyl-2,5-pyrazinedicarboxylate was prepared by the oxidation [22] of 2,5-dimethylpyrazine with SeO₂ to the dicarboxylic acid and subsequent esterification. Samples were introduced to the mass spectrometer either via an all-glass heated inlet system equipped with a leak valve or a direct insertion-type probe having a glass bore and reservoir. At indicated pressures (monitored by a remote ionization gauge) of typically 10⁻⁶ Torr, ions were formed by electron ionization (70 eV) with the source temperature at 120 °C.

4. Results and discussion

4.1. Computations

The computational strategy is very similar to the one described earlier for the related hydrogen shift isomers of pyridine [9,14] and the discussion can therefore be kept brief. Stable structures were computed for **1–5** as neutral molecules and radical cations. The computed total and zero-point vibrational energies are summarized together with the relative energies in Table 1. The B3LYP/TZVP derived neutral

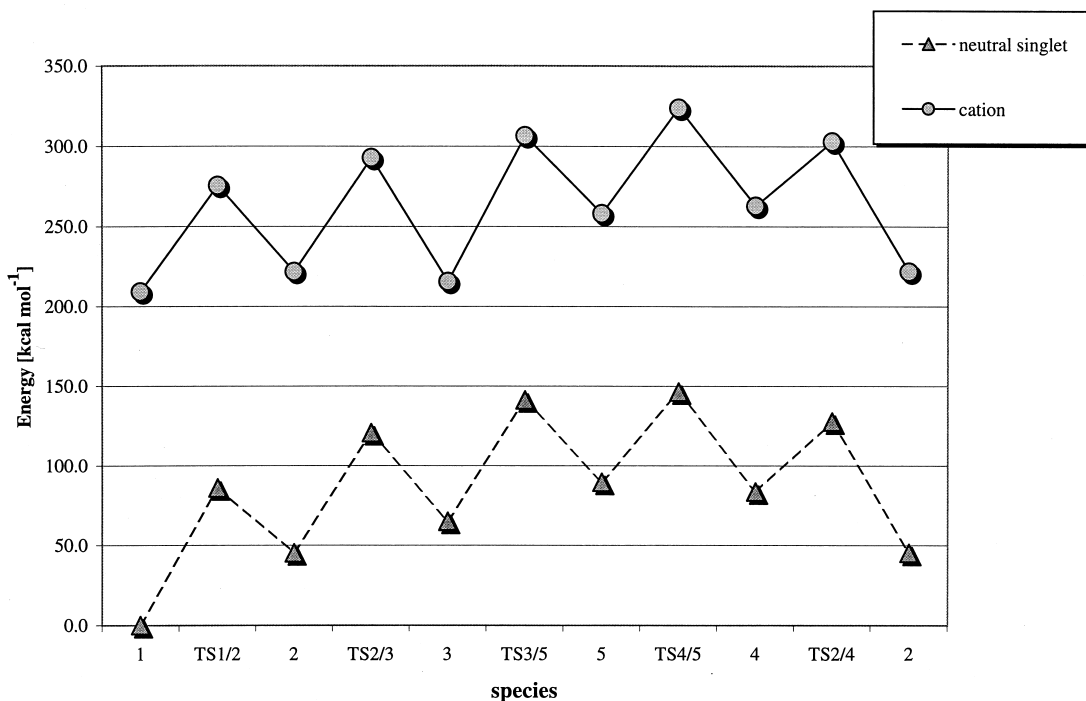


Fig. 1. Potential energy surface for $[C_4H_4N_2]$ and $[C_4H_4N_2]^+$ as computed at B3LYP/TZVP.

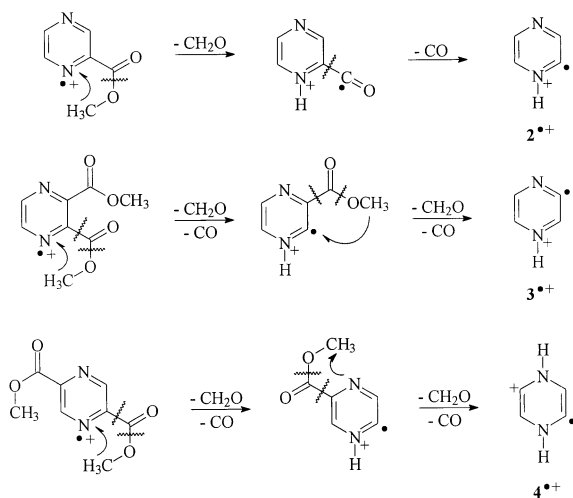
and ionic $[C_4H_4N_2]$ potential energy surfaces are depicted in Fig. 1.

As expected, pyrazine is the most stable species on the neutral potential energy surface [23]. For the ylides **2** and **3**, the B3LYP energy differences with respect to **1** amount to 45.2 and 65.0 kcal mol⁻¹ using the TZVP basis set. For the less stable diradicals **4** and **5**, elevations above **1** of 83.5 and 89.6 kcal mol⁻¹, respectively, are obtained. The ground state singlet **1** (¹A_g) is calculated to be 70.8 kcal mol⁻¹ more stable than the lowest lying triplet state (³B_{3u}), compared to an experimental value of 76.7 kcal mol⁻¹ [24]. For **2**, that is pyrazine-2-ylidene, the singlet-triplet energy gap is much smaller amounting to only 29.1 kcal mol⁻¹. By comparison, this energy difference is 35.6 kcal mol⁻¹ for the pyridine-2-ylidene [9] and 78 kcal mol⁻¹ for the imidazol-2-ylidene [25]. As radical cations, the isomers are more similar in stability, akin to the results obtained recently for the hydrogen shift isomers of pyridine [14]. The radical cation of pyrazine, **1**⁺ still represents the most stable isomer, but

is followed by **3**⁺ (6.6 kcal mol⁻¹), **2**⁺ (12.7 kcal mol⁻¹), **4**⁺ (52.7 kcal mol⁻¹), and finally, **5**⁺ (49.1 kcal mol⁻¹). As indicated in Fig. 1, there are large barriers connected to the [1,2] hydrogen shift transition states interconnecting the various isomers. In all cases, be it the neutral or the cationic potential surface, these barriers are higher than 40 kcal mol⁻¹. Thus, our calculation predicts that the unimolecular spontaneous isomerization into the lowest energy isomer **1** or **1**⁺ will be hindered and under appropriate conditions all these species should be observable in the gas phase.

4.2. Mass spectrometry

Pyrazine and several of its derivatives have been investigated using tandem mass spectrometry methods [26] in our attempt to generate and characterize the $[C_4H_4N_2]$ isomers that the computations predicted would be stable in both their cationic and neutral forms. Generation of **1**⁺ is easily accom-



Scheme 2. Routes that would generate (a) 2^+ from ionized methyl-2-pyrazinecarboxylate, (b) 3^+ from ionized dimethyl-2,3-pyrazinedicarboxylate, and (c) 4^+ from ionized dimethyl-2,5-pyrazinedicarboxylate.

published by electron ionization (EI) of pyrazine [27]. The other isomeric structures 2^+ , 3^+ , and 4^+ were anticipated from the methyl esters of pyrazine-2-carboxylic acid, pyrazine-2,3-dicarboxylic acid, and pyrazine-2,5-dicarboxylic acid, respectively, as summarized in Scheme 2 [9,14,28]. The structures of these potentially isomeric ions were first probed by metastable ion (MI) and collision-induced dissociation mass spectrometry experiments. The metastable ion results are summarized in Table 2 and the CID mass spectra are shown in Fig. 2.

Pyrazine has been the subject of many mass spectrometry based investigations and a great deal of information is available about the ionization of 1^+

[27,29]. For 1^+ the dissociation reaction of lowest energy requirement is loss of HCN [30]. In fact, the MI mass spectrum of each isomer is dominated by a peak at m/z 53 that corresponds to [C,H,N] elimination. However, we measured the kinetic energy release values ($T_{0.5}$) for the m/z 53 peaks [31] and found that they were not the same for all the ions (Table 2, values in parentheses). The differences reveal that 1^+ is certainly distinguishable from its isomers prior to loss of [C,H,N], which is in agreement with the computed barrier height, $\text{TS}1^+/2^+$. Furthermore, neither of these metastable ions communicate with the ion 4^+ ; this is the only isomer that cannot eliminate HCN directly and it has the highest ratio of m/z 52 to m/z 53. Both 2^+ and 3^+ can eliminate HCN directly, and the barrier separating them is predicted by the calculations to be quite a bit higher than $\text{TS}1^+/2^+$, so the identical $T_{0.5}$ values for the ions from the methyl esters of pyrazine-2-carboxylic acid and pyrazine-2,3-dicarboxylic acid might be an unusual coincidence. Alternatively, it could be indicative that 2^+ and 3^+ share a common (excited state) dissociation pathway or intermediate [31]. Discerning between these various possibilities would seem to require other types of experiments than ours [32].

In CID experiments, the collision event gives the ions enough internal energy to isomerize but commonly dissociation takes place even more rapidly, i.e. before isomerization occurs. Thus, the differences between isomeric ions are more often manifested in CID mass spectra than MI mass spectra. However, gross spectral differences may not show up for collisionally activated ions 1^+ – 4^+ since their basic similarity in ring structure leaves few unique dissociation channels available to the isomeric ions. Indeed, the CID mass spectra of the $\text{C}_4\text{H}_4\text{N}_2^+$ ions are similar to one another, but completely different from other known acyclic isomers [33]. However, an examination of the spectra in Fig. 2 leaves no doubt that the m/z 80 ions from the esters are not pyrazine radical cations 1^+ . The latter ions are characterized by an intense m/z 26 fragment ion, consistent with the presence of the acetylene moiety (HCCH) embedded in the pyrazine ring. Furthermore, certain peaks are

Table 2
Metastable ion mass spectra of $\text{C}_4\text{H}_4\text{N}_2^+$ ions

$\text{C}_4\text{H}_4\text{N}_2^+$ ion	1^+	2^+	3^+	4^+
53	100	100	100	100
($T_{0.5}$) ^a	(22.8)	(36.2)	(36.2)	(30.8)
52	2	5	10	20
29	—	—	—	2
28	—	2	4	3
26	2	2	3	—

^a $T_{0.5}$ values are in meV and refer to the peak at $m/z = 53$ (loss of C,H,N).

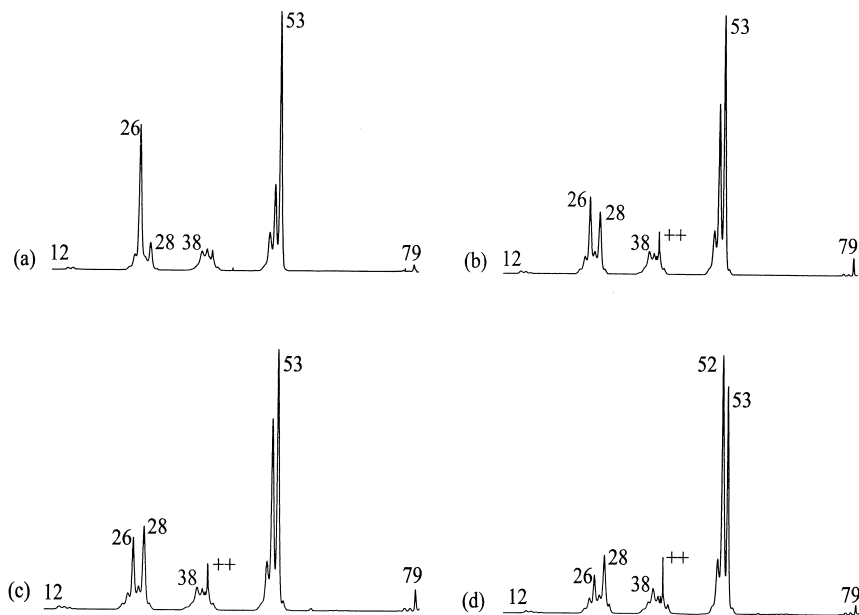


Fig. 2. CID mass spectra of $[C_4H_4N_2]^+$ ions (m/z 80) generated from ionized (a) pyrazine, (b) methyl-2-pyrazinecarboxylate, (c) dimethyl-2,3-pyrazinedicarboxylate, and (d) dimethyl-2,5-pyrazinedicarboxylate.

notably weak or by comparison they are more prominent in the spectra of the other isomer(s) e.g. m/z 28 ($HNCH^+$) and the doubly-charged ions at m/z 39.5 and m/z 40 that arise from charge-stripping. It should be noted though that the diagnostic use of the m/z 38–40 region is complicated by the juxtaposition of CID and charge-stripping peaks. Finally, the very weak cluster at m/z 12–15 appears to signal the presence or absence of C, CH, N, and NH units to some extent. Even with these points in mind, the assignment of structures to the ions of Fig. 2 (b)–(d) is challenging. However, the latter spectrum does show features consistent with the structure of ion 4^{++} that would presumably rapidly oust the extant H–N=C–H segments as either charged or neutral fragments (loss of 28 u). In accordance with this, we note that m/z 52 is more intense than m/z 53 (loss of HCN/HNC) and the ratio of m/z 26:28 is the smallest for the ions formed from the 2,5-diester. According to the pathway suggested in Scheme 2, the m/z 81 ions of composition $C_4H_3DN_2$ produced from the CD_3 labeled monoester derivative of pyrazine should have the deuterium atom bonded to the nitrogen atom. If

the unlabeled compound yielded ions 2^+ then these m/z 81 ions should be α -ylide cations that are isotopically substituted with deuterium on the nitrogen atom, which could be expected to fragment preferentially to $HCND^+$ (m/z 29), and other characteristic species. Indeed, the peak at m/z 28 has largely shifted to m/z 29 in the CID spectrum of the labeled ions but it is not feasible to assess the extent of hydrogen-deuterium (H/D) mixing prior to dissociation from an analysis of only these two spectra.

The neutralization reionization mass spectra of the ions from the four precursors appear in Fig. 3. They all contain abundant recovery signals at m/z 80 corresponding to stable $C_4H_4N_2$ molecules. It is further apparent that the NR mass spectra differ from one another, although their lack of close resemblance to the individual CID mass spectra makes any definitive statement about the neutral structures untenable at this juncture. The structural evidence provided by the m/z 12–15, 26, 28, 52, and 53 intensities is limited, not altogether uninformative. For instance, the intense m/z 26 peak is featured again after NR of 1^+ and the m/z 52:53 ratio is still unique after NR of

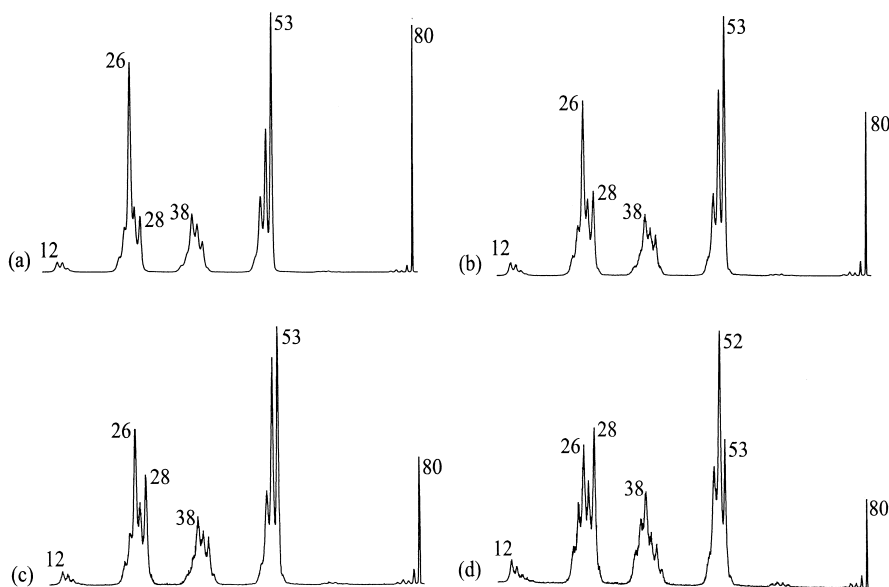


Fig. 3. NR mass spectra of m/z 80 ions generated from ionized (a) pyrazine, (b) methyl-2-pyrazinecarboxylate, (c) dimethyl-2,3-pyrazinedicarboxylate, and (d) dimethyl-2,5-pyrazinedicarboxylate.

4^+ . However, the NR mass spectra of 2^+ and 3^+ are more similar to each other than their CID spectra. Some of the uncertainties in structure assignment can be obviated by obtaining the CID mass spectra of only the recovery ions, i.e. those m/z 80 ions that survived the process: $C_4H_4N_2^+ \rightarrow C_4H_4N_2 \rightarrow C_4H_4N_2^+$. The advantages and constraints of this approach have been previously discussed [9, 10].

For direct comparison, each NR/CID mass spectrum of reionized $C_4H_4N_2$ neutrals is shown paired with its corresponding third field-free region CID mass spectrum of source generated m/z 80 ions in Fig. 4. A decisive trait shared by all sets is that each NR/CID spectrum is similar to the CID spectrum. The spectra of pyrazine ions are immediately distinguishable among the four sets of spectra. It also becomes apparent from an inspection of the pairs of spectra that the other ions still differ from one another after NR. The sets of spectra display characteristic m/z 26:28 ratios and except for the ions from dimethyl-2,3-pyrazinedicarboxylic acid they are the same within experimental uncertainty. As has been argued before [9], this similarity implies that the primary ion beam consisted almost entirely of a single isomeric species

that was neutralized and reionized without inducing isomerization of a substantial fraction of the ion or neutral population. The situation is more complicated for the ions from the remaining precursor since they appear to be altered following neutralization and reionization. The MI and CID peak ratios, especially 26:28:38, ensure that we have been dealing with at least four $C_4H_4N_2^+$ isomers. However, the m/z 80 ion flux obtained from dimethyl-2,3-pyrazinedicarboxylic acid may not be pure, i.e. consist of a single isomer. Simultaneous cogeneration of 1^+ (a small amount) or 2^+ could explain the increase in m/z 26 following NR. Alternatively, the possibility that a portion of the ions 3^+ can isomerize to 1^+ or 2^+ after NR could be entertained. However, the stability of 3^+ and the high barriers (see above) make this less attractive than the cogeneration option. Could neutrals **3** isomerize as well or instead? Remarkably, the β -ylide S_0 and T_0 energy surfaces are almost isoenergetic and the calculations indicate that Franck–Condon type reduction actually favors entry to the triplet state manifold. However, in neither case would ground state ions produce neutrals with sufficient energy to isomerize. Furthermore, the deep energy well on the ionic

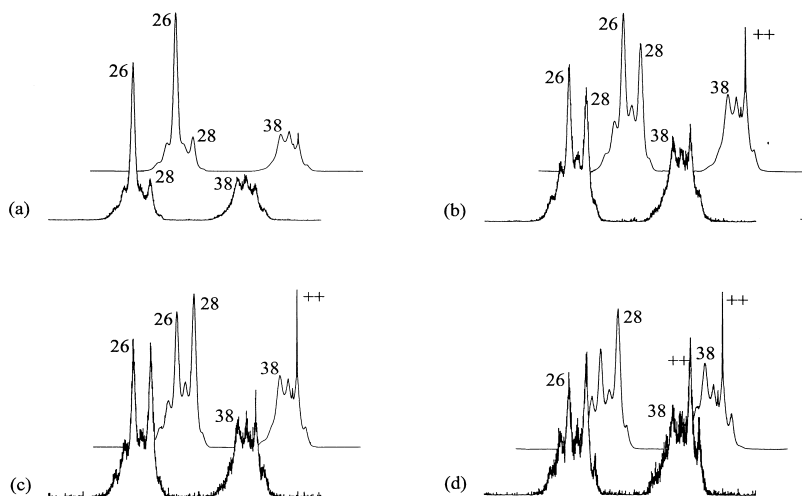


Fig. 4. NR/CID mass spectra (front) and comparative CID mass spectra (back) of the m/z 80 ions generated from ionized (a) pyrazine, (b) methyl-2-pyrazinecarboxylic acid, (c) dimethyl-2,3-pyrazinedicarboxylic acid, and (d) dimethyl-2,5-pyrazinedicarboxylic acid.

surface makes it unlikely that reionization from either state would give ions 3^+ that isomerize. To gain further insight another experiment was performed. The m/z 80 ions that were produced by the spontaneous loss of CO from m/z 108 ions generated by dimethyl-2,3-pyrazinedicarboxylic acid in the ion source were subjected to CID. The resulting (MI/CID) mass spectrum (not shown) was compared with the CID mass spectrum of source generated m/z 80 ions having the appropriate velocity. The metastable m/z 108 precursor ions will have a narrow distribution of internal energy and in fragmentation favor the production of the most stable products. The product m/z 80 ions in the MI/CID experiment are expected to be relatively cold and would only be able to isomerize post-collision. The MI/CID mass spectrum showed an increased m/z 26:28 ratio that is thus consistent with the cogeneration hypothesis wherein a small proportion ($\sim 10\%$) of 1^+ is formed along with 3^+ .

In summary, a combination of tandem mass spectrometry experiments and quantum chemical calculations have allowed the generation and characterization of three new isomers of pyrazine as their solitary radical cations and neutral molecules. It is hoped that this study will provide impetus for future spectroscopic and matrix isolation studies.

Acknowledgements

The Natural Sciences and Engineering Research Council (NSERC) of Canada supported the work at McMaster University and granted D.J.L. a Postgraduate Scholarship (McMaster) and awarded G.A.M. a Post Doctoral Fellowship (TU Berlin). The research at the TU Berlin was funded by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. Computing resources were generously provided by the Konrad-Zuse Zentrum für Informationstechnik, Berlin.

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