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Generation of neutral and cationic hydrogen shift isomers of pyridine: a combined experimental and computational investigation

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Abstract

Azacyclohexatriene-3-ylidene **(3)**, an isomer of pyridine **(2)** and its previously generated Hammick intermediate **(1)**, is accessible in the gas phase by one-electron reduction of the corresponding radical cation in neutralization-reionization mass spectrometric experiments. The experimental finding that this carbene is stable on the microsecond time scale is in agreement with results of quantum chemical calculations, which indicate that all these C_5H_5N and $C_5H_5N^{\cdot +}$ isomers, including also the isomers of azacyclohexatriene-4-ylidene **4** and $\mathbf{4}^{\cdot +}$, correspond to minima that are separated by significant barriers, thus preventing facile unimolecular isomerization. Although neutral pyridine is much more stable than the ylidic carbenes **1**, **3**, and **4**, for the radical cations the $C_5H_5N^{\cdot +}$ isomers are nearly isoenergetic, with $\mathbf{4}^{\cdot +}$ actually being lowest in energy. (Int J Mass Spectrom 179/180 (1998) 7–14) © 1998 Elsevier Science B.V.

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1. Introduction

There are many simple molecules that have been studied by computational methods sufficiently often and thoroughly enough that they take on an aura of familiarity but nevertheless still manage to elude experimental observation. Among the most famous of these is OCCO [1]; other candidates for such reactive intermediates are carbenes whose generation and identification have received a great deal of attention during the past decades [2,3]. A case in point concerns the hydrogen-shift isomers **1**, **3**, and **4** of pyridine **(2)**. The 2-isomer of pyridine [i.e. azacyclohexatriene-2-ylide **(1)**] was postulated to exist more than 60 years ago by Hammick and co-workers [4,5]; however, unequivocal evidence for its gas-phase existence was presented only recently [6]. Although there is neither experimental nor theoretical support in favor of **4**, convincing data for the intermediary formation of **3** in

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Dedicated to Professor Fulvio Cacace in recognition of his pioneering and stimulating work on gas-phase ion chemistry and physics.

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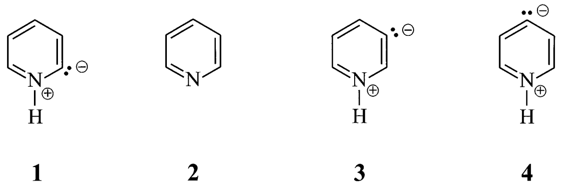


Chart

the reaction of gaseous atomic carbon with pyrrole was recently obtained [7]; however, very facile intermolecular isomerization **3** → **1** → **2** is operative in solution [7,8].

Quite clearly, despite the enormous progress made in the study of these elusive species in condensed phases, there are often advantages, especially for molecules that are susceptible to intermolecular isomerizations (or dimerization), to conduct investigations under high vacuum conditions in the gas phase where intermolecular reactions are virtually absent. Mass spectrometric experiments often provide an opportunity, and following the introduction of neutralization-reionization mass spectrometry (NRMS) [9–12], the technique has proved valuable in generating a great variety of remarkable molecules, including several carbenes (e.g. **1** [6], $H_2N–C–NH_2$ [13], $H_2N–C–OH$ [14–16], $H_3C–C–OH$ [17], F–C–OH [18], and H–C–OH [19,20]), that are expected to have only a fleeting existence in solution. In addition, the often invoked and long-sought-after cyclic heterocarbenes (i.e. 3H-thiazole-2-ylidene [21] and imidazol-2-ylidene [22]) were generated by one-electron reduction of their corresponding radical cations and characterized by NRMS in conjunction with electronic structure calculations.

Inspired by these findings, we set out to generate and identify the elusive carbene **3** (Chart 1), using the combined experimental (NRMS) and computational methodology described in detail in our previous study of the Hammick intermediate **1** [6]. This strategy to combine ingenious experimental techniques with powerful computational methods is of particular importance in cases where the spectra of the various species differ only in subtle details. If this experimental information is not backed by other, independent pieces of evidence, it may not suffice for an unequivocal identification of structurally distinct ions. However, if these experimental data are complemented with high-quality calculations, reliable conclusions about the system at hand can be drawn.

2. Theoretical and experimental

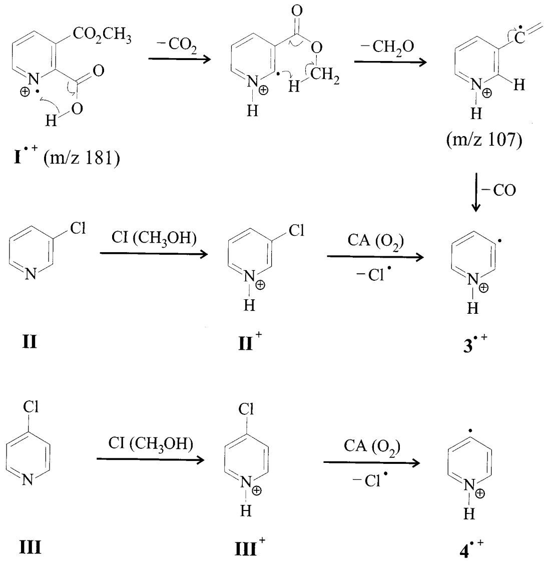
The computational determinations of the structures and harmonic frequencies were performed on IBM/RS6000 workstations using the Gaussian 94 program package [23]. The popular B3LYP hybrid density functional theory (DFT) [24] option employing Becke's [25] empirical three-parameter fit for mixing HF and DFT exchange-energy terms as implemented [26] in Gaussian 94 was combined with the standard 6-31G** basis set [27], which includes d- and p-type polarization functions on non-hydrogen and hydrogen atoms, respectively. All relative energies were corrected for zero-point vibrational energy (ZPVE) contributions. No scaling was performed for the B3LYP fundamentals. Open shell species were treated in the unrestricted Kohn-Sham scheme. The $\langle S^2 \rangle$ expectation values of the noninteracting Kohn-Sham determinant did not exceed 2.037 for the triplet states (exact value = 2.00) and 0.771 for the doublet states (exact value = 0.75). The only species that had a larger spin contamination was $\mathbf{TS1}^{\cdot +}/\mathbf{2}^{\cdot +}$ where $\langle S^2 \rangle$ amounts to 0.876. Improved relative energies based on these optimized structures were obtained by using the coupled cluster ansatz with single and double excitations and a perturbative estimation of the triple excitations [CCSD(T)] [28–30] to account for the effects of valence electron correlation. For these calculations the MOLPRO96.4 computer program [31] implemented on a Cray J90 computer at the Konrad-Zuse Zentrum für Informationstechnik, Berlin, was employed. The CCSD(T) method was combined with a more flexible, generally contracted, basis set of the atomic natural orbital (ANO) type [32] of polarized triple zeta quality (H: $[7s3p]/(3s2p)$, N, C: $[10s6p3d]/(4s3p2d)$) [33]. Thus, the final basis set, which will be termed ANO-TZP in the following text, consists of 356 primitive Gaussians and 183 contractions. For the open shell species, the CCSD(T) calculations were based on ROHF wave functions, as implemented in MOLPRO96.4. The CCSD(T)/ANO-TZP relative energies are corrected for ZPVE contributions by using the harmonic fundamentals as obtained at the B3LYP/6-31G** level of theory. For further details, see Lavorato et al. [6].

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 NR mass spectra have been previously described [34]. Briefly, the NR experiments were performed on mass-selected ions between the magnet (B) and the first electric sector (E) of the BE_1E_2 geometry ZAB-R. There are two small gas cells in this region: the first pressurized with *N*,*N*-dimethylaniline to enable electron transfer neutralization of a fraction of the 10 kV source generated ions and the second containing oxygen for collisional reionization of the neutral particles. In between is a positively charged deflector electrode to ensure that only neutral molecules enter the second cell. The spectra are recorded with a PC-based data system (Mommers Technologies, Ottawa, Canada) by scanning E_1. Collisional activation (CA) mass spectra were obtained in the same region with the first cell empty and the deflector switched off. The NR/CA (see text) and CA mass spectra were obtained, using oxygen as a collision gas present in another cell between E_1 and E_2, by scanning the latter sector with the former set at a fixed potential.

3. Results and discussion

3.1. Mass spectrometry

The proper identification of neutral species by NRMS requires that one be able to unambiguously establish the parent ion structure. As shown earlier [6], this search was quite brief and successful for the isomeric ions **1**$^{\cdot +}$ and **2**$^{\cdot +}$. The molecular ion **2**$^{\cdot +}$ is undoubtedly generated by electron ionization of **2**, whereas carbene ion **1**$^{\cdot +}$ is accessible by consecutive loss of CH_2O and CO from ionized methyl picolinate. Based on labelling experiments, kinetic energy release analyses, and collisional activation studies, both isomers are clearly distinguishable. Of particular importance were the minor but structure-indicative differences in the CA mass spectra. The most critical of these are the *m*/*z* 28:*m*/*z* 26 ratio and the doubly charged ion intensities. In the comparison of **1**$^{\cdot +}$ and **2**$^{\cdot +}$, only **1**$^{\cdot +}$ possesses a hydrogen on the nitrogen atom. It should therefore be able to produce the *m*/*z* 28 ion ($HCNH^+$) [35,36] more easily than **2**$^{\cdot +}$, whereas both isomers can give *m*/*z* 26 fragments ($C_2H_2^{\cdot +}$ and CN^+). Furthermore, in the CA mass spectrum of $C_5H_4DN^{\cdot +}$ (*m*/*z* 80) generated from ionized 2-CD_3-methyl picolinate the *m*/*z* 28 signal is also shifted to *m*/*z* 29 ($HCND^+$). These features were also preserved in the NR/CA spectra of **1**$^{\cdot +}$, **2**$^{\cdot +}$, and the N—D labelled isotopologue of **1**$^{\cdot +}$, thus demonstrating that irrespective of their charge states the two isomers do not easily interconvert, as predicted by extensive electronic structure calculations [6].



Scheme 1.

For the isomer in question, **3**$^{\cdot +}$, a related strategy was pursued. Upon electron ionization (EI), methyl-2-carboxypyridine-3-carboxylate **I** [37] undergoes consecutive loss of CO_2, CH_2O, and CO (Scheme 1); the resulting *m*/*z* 79 ions may well have the ionized 3-ylidene structure **3**$^{\cdot +}$ desired for the NR experiment. To verify the isomeric purity of the putative β-distonic ion $\mathbf{3}^{\cdot +}$ generated from $\mathbf{I}^{\cdot +}$, these ions were independently produced by the reaction sequence shown in Scheme 1, that is from ion-source generated protonated 3-chloropyridine **II** [chemical ionization (CI) of **II** with methanol]; ions at m/z 114 were mass-selected and subsequently collisionally decomposed in the second field-free region (2ffr). The isomeric γ-distonic ion $\mathbf{4}^{\cdot +}$ was prepared analogously (i.e., via protonation of 4-chloropyridine **III**). Unfortunately, no suitable precursor molecule could be found to generate ion $\mathbf{4}^{\cdot +}$ by EI, and therefore its neutral counterpart could not be studied by NRMS using the ZAB-R.

As argued before [6], a distinction of ionized pyridine $\mathbf{2}^{\cdot +}$ from its isomer $\mathbf{1}^{\cdot +}$ is readily available on the basis of the m/z 28:m/z 26 intensity ratio in their CA mass spectra. Fig. 1(a) and (b) represent the structure-diagnostic portions of the CA mass spectra of $\mathbf{1}^{\cdot +}$ and $\mathbf{2}^{\cdot +}$, respectively. As reported earlier, isomer $\mathbf{1}^{\cdot +}$ is characterized by a m/z 28:m/z 26 peak intensity ratio of 0.86 ± 0.03, whereas fewer $HCNH^+$ ions at m/z 28 are generated from $\mathbf{2}^{\cdot +}$ (intensity ratio 0.41 ± 0.03). Note that the CA spectra also show intensity ratio differences in the m/z 37–39 region and that the ylide ion $\mathbf{1}^{\cdot +}$ features a pronounced doubly charged ion of m/z 39.5 that is virtually absent in the CA mass spectrum of ionized pyridine ($\mathbf{2}^{\cdot +}$).

Fig. 1(c) and (d) represent the structure diagnostic portions of the CA spectra of the isomeric m/z 79 $C_5H_5N^{\cdot +}$ ions of putative structure $\mathbf{3}^{\cdot +}$ generated from **I** and **II**, respectively, as depicted in Scheme 1. The two spectra are the same within experimental error and their m/z 28:m/z 26 ratio, 1.99 ± 0.04, is characteristically different from that of both $\mathbf{1}^{\cdot +}$ and $\mathbf{2}^{\cdot +}$, attesting to the generation of the β-distonic ion $\mathbf{3}^{\cdot +}$. In agreement with this proposal, the CA mass spectrum of the m/z 80 $C_5H_4DN^{\cdot +}$ ions from the OD labelled isotopomer of the ionized ester **I** shows a clean shift of the m/z 28 $HCNH^+$ signal to m/z 29, $HCND^+$. That the β-distonic ions generated by the pathways depicted in Scheme 1 are isomerically "pure" is further attested by the observation that the m/z 79 $C_5N_5N^{\cdot +}$ ions generated by the loss of CO

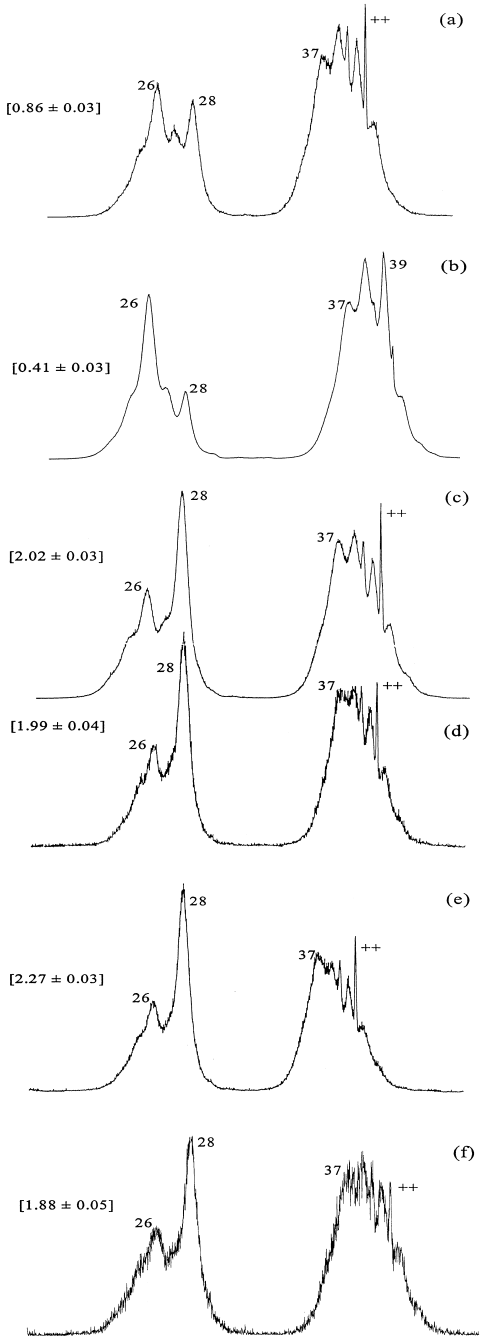


Fig. 1. Partial CA mass spectra of ionized pyridine$^{\cdot +}$ and its hydrogen shift isomers: (a) ionized pyridine-2-ylidene, $\mathbf{1}^{\cdot +}$; (b) ionized pyridine, $\mathbf{2}^{\cdot +}$; (c) and (d) ionized pyridine-3-ylidene, $\mathbf{3}^{\cdot +}$, generated from **I** and **II**, respectively (see Scheme 1); (e) ionized pyridine-4-ylidene, $\mathbf{4}^{\cdot +}$; and (f) NR/CA spectrum of the survivor ions from $\mathbf{3}^{\cdot +}$. See text for further details.

Table 1
Calculated energies for selected C_5H_5N neutral species, radical cations, and transition structures for 1.2-hydrogen migrations[a,b]

Species	Symmetry/state	ZPVE (kcal mol^{-1})	E_{rel} (kcal mol^{-1})[c]	
			B3LYP/6-31G**	CCSD(T)/ANO-TZP
1 (singlet)	$C_s\,^1A'$	55.6	46.8	43.4
TS **1**/**2** (singlet)	$C_s\,^1A'$	51.3	85.1	85.5
2 (singlet)	$C_{2v}\,^1A_1$	55.8	0.0[a]	0.0[b]
TS **1**/**3** (singlet)	$C_1\,^1A$	51.3	120.2	118.6
3 (singlet)	$C_s\,^1A'$	54.8	61.2	57.8
TS **3**/**4** (singlet)	$C_s\,^1A'$	51.3	127.5	126.6
4 (singlet)	$C_{2v}\,^1A_1$	55.1	63.1	59.6
1 (triplet)	$C_1\,^3A$	53.3	82.4	83.5
TS **1**/**2** (triplet)	$C_1\,^3A$	49.4	133.8	135.7
2 (triplet)	$C_1\,^3A$	52.3	81.8	84.0
TS **1**/**3** (triplet)	$C_1\,^3A$	49.9	131.9	136.3
3 (triplet)	$C_1\,^3A$	52.7	81.6	82.9
TS **3**/**4** (triplet)	$C_1\,^3A$	49.7	138.9	141.6
4 (triplet)	$C_s\,^3A'$	53.4	81.9	82.6
$\mathbf{1}^{\cdot+}$	$C_1\,^2A'$	56.1	204.2	208.1
TS $\mathbf{1}^{\cdot+}/\mathbf{2}^{\cdot+}$	$C_1\,^2A$	54.5	264.3	271.3
$\mathbf{2}^{\cdot+}$	$C_1\,^2A$	54.2	203.1	210.0
TS $\mathbf{1}^{\cdot+}/\mathbf{3}^{\cdot+}$	$C_1\,^2A$	52.0	271.4	277.3
$\mathbf{3}^{\cdot+}$	$C_s\,^2A'$	56.3	203.5	207.4
TS $\mathbf{3}^{\cdot+}/\mathbf{4}^{\cdot+}$	$C_s\,^2A'$	52.1	268.6	274.1
$\mathbf{4}^{\cdot+}$	$C_{2v}\,^2A_1$	56.3	201.3	205.1

[a] $E_{tot} = -248.29260$ hartree.
[b] $E_{tot} = -247.71758$ hartree.
[c] Corrected for ZPVE.

from the low energy (metastable) m/z 107 ions (see Scheme 1) yield essentially the same m/z 28:m/z 26 ratio, 2.02 ± 0.03 (after correcting for the substantial ^{13}C contribution from the transition $m/z\ 106 \rightarrow m/z\ 78 + CO$; result not shown).

The partial mass spectrum of the remaining hydrogen shift isomer of ionized pyridine (i.e., $\mathbf{4}^{\cdot+}$) is shown in Fig. 1(e). This spectrum exhibits the largest m/z 28:m/z 26 ratio, 2.27 ± 0.03, and it also features m/z 37 (C_3H^+) as the most prominent peak in the m/z 37–m/z 39 cluster of ions. Considering the results of our theoretical calculations on the ions (see Table 1, which summarizes our computational findings for the ions $\mathbf{1}^{\cdot+}$–$\mathbf{4}^{\cdot+}$, their neutral counterparts **1**–**4**, and the isomerization barriers separating the various species) it is seen that (1) all four isomeric ions have closely similar stabilities and (2) the barriers separating the ionic isomers are uniformly high, 50–60 kcal/mol. This reinforces our conclusion that the β-distonic ions $\mathbf{3}^{\cdot+}$ are isomerically pure and also that the γ-distonic ions $\mathbf{4}^{\cdot+}$, whose CA mass spectrum is otherwise fairly close to that of $\mathbf{3}^{\cdot+}$, do not effectively communicate with the β-distonic ion $\mathbf{3}^{\cdot+}$.

One-electron reduction of the 6 keV β-distonic ion $\mathbf{3}^{\cdot+}$ from $\mathbf{I}^{\cdot+}$ by neutralization with N,N-dimethylaniline [6] followed by reionization with O_2 yields a NR mass spectrum dominated by a survivor ion at m/z 79. These ions were selectively transmitted to the 3ffr and subjected to CA using O_2. The resulting survivor CA mass spectrum is given in Fig. 1(f) and its close similarity with the CA mass spectra of the ions $\mathbf{3}^{\cdot+}$ [Fig. 1(c) and (d)] leaves little doubt that most neutralized ions $\mathbf{3}^{\cdot+}$ have retained their structural integrity and thus that pyridine-3-ylidene **3** is indeed a stable species in the gas phase. This conclusion is fully corroborated by our calculations (Table 1).

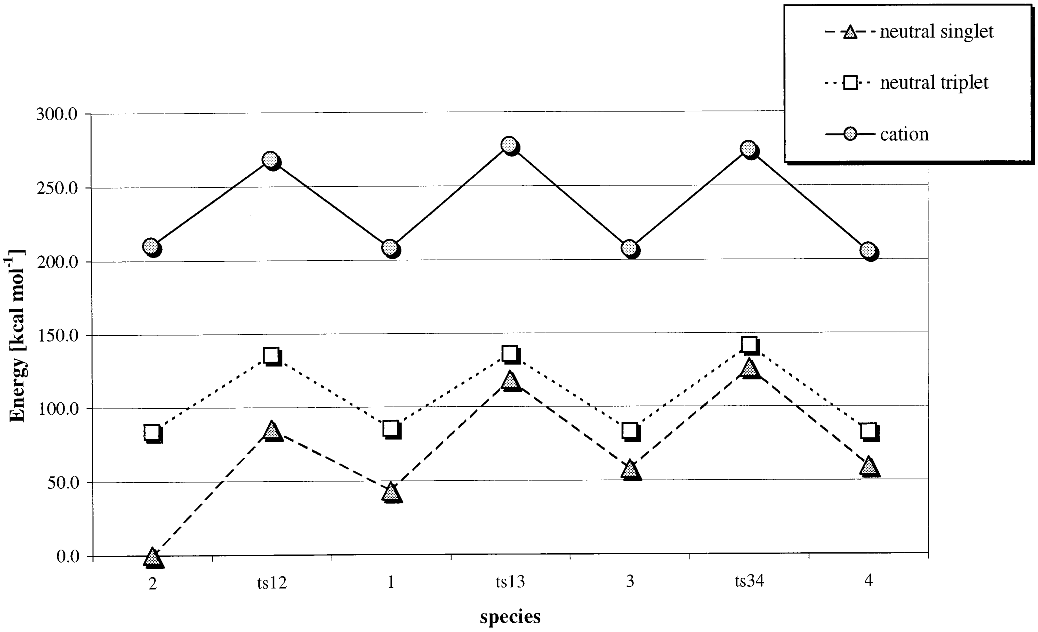


Fig. 2. Schematic potential energy surface [CCSD(T)/ANO-TZP//B3LYP/6-31G**] for neutral and cationic C_5H_5N isomers. Relative energies are given in kcal mol^{-1}. Detailed geometries of all species are available upon request from thda0531@argon.chem.tu-berlin.de

3.2. Computations

In view of our previous detailed discussion [6] of the potential energy surfaces (PESs) of **1**, **1**$^{\cdot +}$, **2**, and **2**$^{\cdot +}$ and of related theoretical work on the C_5H_5N-PES [7], as well as for ionized pyridine **2**$^{\cdot +}$ [38–42], a brief presentation of our present theoretical findings (summarized in Table 1 and Fig. 2) may suffice. First of all, we note that the B3LYP/6-31G* and CCSD(T)/ANO-TZP energetic data are generally in good agreement. The largest deviation amounts to ~7 kcal mol^{-1}. The quality of the quantitative results can be assessed by a comparison of the experimentally well known adiabatic ionization energy of pyridine (**2**) of 214.9 kcal mol^{-1} with the corresponding value predicted at CCSDC(T)/ANO-TZP and B3LYP/6-31G** of 210.0 and 203.7 kcal mol^{-1}, respectively. Similarly, the experimental T_0 for the $^3B_1 \leftarrow {}^1A_1$ excitation of 84.8 kcal mol^{-1} is well reproduced at CCSD(T)/ANO-TZP (84.0 kcal mol^{-1}), whereas the B3LYP/6-31G* result is slightly smaller (81.8 kcal mol^{-1}). It is a general trend that the singlet/triplet excitation energies, as well as the ionization energies, are consistently larger by ~3–4 and 7 kcal mol^{-1}, respectively, at the CCSD(T)/ANO-TZP level compared with B3LYP/6-31G**.

For neutral, singlet C_5H_5N, pyridine **2** is by far the most stable species, followed by **1** [43.4 kcal mol^{-1}, CCSD(T)]. The isomers **3** and **4** are higher still, almost 60 kcal mol^{-1} above **2**. However, significant activation barriers hinder the unimolecular, spontaneous isomerization into pyridine. The lowest of these barriers is between **1** and **2** and is still more than 40 kcal mol^{-1} above **1**. For the triplets and the cationic ($S = 1/2$) species, there is no isomer with a comparably unique energetical advantage as pyridine for the neutral singlets. All four isomers (i.e., the triplets of **1**–**4** and the radical cations **1**$^{\cdot +}$–**4**$^{\cdot +}$) are almost isoenergetic: their relative stabilities differ by not more than 1.4 and 4.9 kcal mol^{-1} for the neutral triplets and the cationic doublets, respectively. The same applies to the barriers for the respective 1,2-hydrogen migrations. They are all of comparable height, between 50 and 60 kcal mol^{-1} on both PESs.

Furthermore, we note that on all three PESs, **1–4** are genuine minima with positive definite Hessian matrices.

Finally, the large barriers to isomerization, indicated by the computational and experimental results, clearly point to the possibility of directly observing the ylide isomers of pyridine (i.e. **1**, **3**, and **4**) in the condensed phase under appropriate conditions (e.g. by low temperature matrix isolation). As already pointed out by Shevlin and co-workers [7,8], direct observation in solution is more problematic because of facile, intermolecularly catalyzed isomerizations.

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