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Observation of the Hammick Intermediate: Reduction of the Pyridine-2-ylid Ion in the Gas Phase[†]

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Abstract: Azacyclohexatriene-2-ylidene (**1**), the 2-isomer of pyridine (**2**), has been generated by one-electron reduction of the corresponding radical cation in neutralization−reionization mass spectrometric experiments. The experimental finding that this molecule is stable on the microsecond time scale is in agreement with results of quantum chemical calculations that indicate both **1** and its radical cation, $\mathbf{1}^{\bullet+}$, correspond to minima on the C_5H_5N and $C_5H_5N^{\bullet+}$ potential energy surfaces. The calculations predict that **1** is less stable than pyridine, **2**, by 50 and 49 kcal/mol (MP2/6-31G** and CASSCF-MP2/6-31G**, respectively) or 47 kcal/mol (B3LYP/6-31G**), whereas the radical cations $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ are much closer in energy. The ylid ion $\mathbf{1}^{\bullet+}$ is predicted to be 6 and 7 kcal/mol lower in energy than $\mathbf{2}^{\bullet+}$ at the MP2 and CASSCF-MP2/6-31G** levels, respectively, and 1 kcal/mol higher according to the hybrid density functional theory. Calculations also suggest that facile isomerization of the ions is prohibited by an energy barrier, amounting to 62 and 57 kcal/mol at MP2/6-31G** and B3LYP/6-31G**, respectively, relative to $\mathbf{1}^{\bullet+}$, which is even larger than the 38 kcal/mol obtained at both levels of theory required for the neutral transformation. Despite the substantial impediments, isomerization of excited species is possible since the lowest dissociation channels lie even higher in energy but the experimental observations confirm that neither the ions or neutrals undergo particularly facile isomerization. Using known thermochemical data a value for $\Delta H_f\ (\mathbf{1}^{\bullet+}) = 237 \pm 5$ kcal/mol was obtained from the measured appearance energy, 10.14 eV, of the $C_5H_5N^{\bullet+}$ ion generated from methyl picolinate, which is completely consistent with the theoretical predictions of 237−242 kcal/mol derived from the calculated energy differences between the various species and the known heat of formation of **2**.

Introduction

A century ago, Nef[1] made clear his desire to prepare carbenes, and since then they have certainly done anything but languish in obscurity.[2,3] Undoubtedly though, fresh impetus for their further study was provided by the exciting reports of remarkably stable compounds that contain dicoordinate carbon centers.[4,5] Not surprisingly, the question as to which features serve to stabilize (singlet) carbenes was considered long before these reports.[6−8] In addition to considering the parent imidazol-2-ylidene, it was suggested that the 2-isomer of pyridine, i.e., **1**, and other polyene type systems should be stabilized by p-π splitting.[8] Even before this, Hammick[9] and co-workers actually postulated the existence of **1**, in its ylidic form **1a**, to explain the accelerated decarboxylation rate of 2-picolinic acid,[10] a reaction which continues to elicit interest,[11] although it was Breslow[12] who first explicitly depicted **1** as being stabilized by the carbene resonance contributor. It seems apparent that a rigorous modern analysis of such reactive intermediates benefits from the wide array of theoretical and experimental methods now available to probe and compare their physical and chemical properties. For example, in the case of the imidazol-2-ylidene type carbenes[13] such an analysis even extends to a comparison with related compounds,[14] which, for example, includes the saturated imidazolin-2-ylidenes,[6,15] silylenes (stable analogues of the imidazol-2-ylidene having been recently discovered[16]),

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[†] Dedicated to Prof. Chava Lifshitz, Jerusalem, on the occasion of her 60th birthday.

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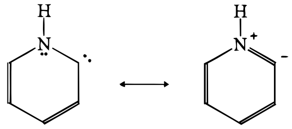
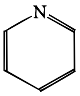
and the phosphorus containing ylides synthesized by Bertrand and co-workers.[17]



1 **1a**



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Despite the enormous progress wrought in the study of such species in condensed phases, there are often advantages, especially for species, that are susceptible to bimolecular tautomerization or dimerization, to conduct investigations in the gas phase, particularly in high vacuum where intermolecular interactions are virtually absent. The interior of a mass spectrometer offers such an environment and following the introduction of the neutralization−reionization mass spectrometry (NRMS)[18] technique it has proved to be an ideal place to study a great variety of species, including several carbenes, e.g., H_2N-C-NH_2,[19] H_2N-C-OH,[20] H_3C-C-OH,[21] F-C-OH,[22] H-C-OH,[23] and ylides, e.g., $H-C^{-}=N^{+}=NH$[24] and $H-C^{-}=N^{+}=CH_2$,[25] that are expected to have only a fleeting existence in solution. One of the advantages of NRMS is that the neutral molecules are accessed by a Franck−Condon type electron transfer to their ionic counterparts, which may be available through the dissociative ionization of a suitable precursor molecule. In the case of the 2-isomer of pyridine, Chen provided strong circumstantial evidence that the radical cation $\mathbf{1}^{\bullet+}$ is formed in this way from 2-picolinic acid as well as its methyl and ethyl esters.[26] It is clear, however, that in order to unambiguously establish the formation of a carbene in a NRMS experiment it is usually necessary to demonstrate that the initial ion beam is not contaminated with interfering ions, i.e., species isomeric or isobaric with the ion of interest. Considerable benefits (not the least of which is the chance to assess the purity of the main ion beam) accrue when it is possible to directly probe the structure, usually by collision induced dissociation (CID), of those ions that survive the neutralization−reionization (NR) process. Furthermore, for both neutral and ionized species there must be energy barriers of sufficient magnitude to prevent the facile equilibration of the carbene with its isomer(s). Sufficiently high level quantum chemical calculations are often an excellent way to obtain insight on the kinetic stability of individual molecules. There is, however, no computational information about the height of the barriers to tautomerization in the present system although Grigg et al. found a stable structure for **1** with Hartree−Fock calculations using the rather limited STO-3G basis set.[27] It is clear though from the ability to trap **1** in solution with aldehydes (giving secondary alcohols) that isomerization by a 1,2-hydrogen shift does not proceed immediately upon its formation. Nyulaszi et al., prompted by the observation of phosphorous ylides,[17] have recently performed computations on the analogous 2-isomer of phosphinine.[28]

We report here the identification of the long-invoked,[8−10,12] but hitherto unobserved, 2-isomer of pyridine by a combination of computational quantum chemistry and mass spectrometry. The structures and stabilities of the two isomeric ions and neutrals and their interconversion barriers were studied by ab initio molecular orbital and hybrid Hartree−Fock/density functional theory calculations. The existence of the two distinct radical cations and the corresponding neutral species was established by collision experiments, in particular, through the use of the neutralization−reionization/collision induced dissociation (NR/CID) technique. Although the possibility of differing descriptive formalism, i.e., carbene or ylide, exists for **1**, we do not concentrate on this aspect in the present work.

Experimental and Theoretical Procedures

The calculations of the structures, energetics, and frequencies were performed on IBM/RS6000 workstations and a CRAY Y-MP using the Gaussian94 program package.[29] Each method employed in this study was combined with the standard 6-31G** basis set,[30] which includes d- and p-type polarization functions on non-hydrogen and hydrogen atoms, respectively. We have considered the effects of valence electron correlation using Møller−Plesset (MP) perturbation theory truncated at second order.[30] For the open shell systems the projected MP2 energy (PMP2), in which the first spin contaminant has been annihilated,[31] has been used for the determination of the relative energies. In addition, for the minimum structures, calculations employing the multireference MP2 procedure based on a complete active space SCF wave function[32] (CASSCF-MP2) as offered in Gaussian94 were performed.[33] The active space consisted of the six π and π* orbitals and the lone pair at nitrogen or carbon, respectively, thus leading to a distribution of eight (seven for the ions) electrons in seven active orbitals. The CASSCF-MP2 energy calculations were based on CASSCF optimized geometries. We have also used the recently suggested B3LYP hybrid Hartree−Fock/density functional theory (DFT)[34] option employing Becke's[35] empirical three-parameter fit for mixing HF and DFT exchange-energy terms as implemented[36] in Gaussian94. All relative energies were corrected for zero-point

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vibrational energy (ZPE) contributions. The ZPE obtained at the MP2 level were uniformly scaled by a factor of 0.9646,[37] while no scaling was performed for the B3LYP fundamentals. For the CASSCF-MP2 energies the ZPE obtained at the MP2 level were used.

The mass spectrometric experiments were performed at McMaster University on the VG Analytical ZAB-R. The details of this instrument and also for the aquisition of NR mass spectra have been previously described.[38] 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 cyclopropane or *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 neutrals. In between is a positively charged deflector electrode to ensure that only neutrals enter the second cell. The spectra are recorded with a PC-based data system (Mommers Technologies Inc., Ottawa, Canada) by scanning E_1. Collision induced dissociation 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, using helium as a collision gas located in another cell between E_1 and E_2, by scanning the latter with the former set at a fixed potential.

The compounds were purchased from commercial sources and used without further purification, except for 2-(D_3-methyl) picolinate, which was obtained by esterification of the acid. 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 resevoir. 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 150 °C.

Results and Discussion

A. Mass Spectrometry. The proper identification of neutral species by NRMS requires that one can confidently establish the parent ion structure. Fortunately, in this case the search for appropriate precursor molecules from which to attempt to generate the isomeric parent ions, $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$, was brief. The carbene ion $\mathbf{1}^{\bullet+}$ was postulated by Chen[26] to explain the differences in the dissociation behavior of $C_5H_5N^{\bullet+}$ ions generated by dissociative 70 eV electron ionization (EI) of various monosubstituted pyridines versus the EI mass spectrum of $\mathbf{2}^{\bullet+}$. The molecular ion $\mathbf{2}^{\bullet+}$ is undoubtedly initially generated by EI of unsubstituted pyridine **2** itself. However, no comparative structural differentiation of the two supposedly distinct isomeric species has been reported despite the fact that the tandem mass spectrometric methods used to accomplish this aim are well-known.[39] This is not a trivial point. The process of lowest energy requirement for pyridine is loss of [H,C,N] with a reported appearance energy $AE(C_4H_4^{\bullet+}) = 13.28$ eV,[40] i.e., the critical energy for the reaction is 4.0 eV. Given this large value, almost 100 kcal/mol, it could reasonably be expected that the $C_5H_5N^{\bullet+}$ isomers are able to interconvert prior to undergoing their unimolecular dissociation. It is not surprising then that the metastable ion (MI) mass spectra of the *m/z* 79 ions obtained by EI of pyridine **2** and by dissociative EI of either picolinic acid or its methyl ester, which we had anticipated to represent ions $\mathbf{2}^{\bullet+}$ and $\mathbf{1}^{\bullet+}$, respectively, are the same. Further evidence of isomerization comes from the MI mass spectrum of the isotopologue of $\mathbf{1}^{\bullet+}$, which was generated from ionized D_3-methyl picolinate by subsequent losses of CD_2O and CO and is thereby initially selectively labeled with a deuterium atom at the nitrogen position. In it, the dominant Gaussian shaped peak in these spectra has split into two components: three parts HCN and one part DCN loss. The situation is not hopeless though, since the collision induced dissociation mass spectra of the *m/z* 79 ions do exhibit minor *but characteristic* differences. The most critical of these are the *m/z* 26:28 ratio and the doubly charged ion intensity. Only $\mathbf{1}^{\bullet+}$ possesses a hydrogen on the nitrogen. It should thus be able to produce the *m/z* 28 ion ($HCNH^+$)[41] more easily than $\mathbf{2}^{\bullet+}$, whereas both ions can give *m/z* 26 fragments ($C_2H_2^{\bullet+}$ and CN^+). For ion $\mathbf{1}^{\bullet+}$, the CID mass spectrum (Table 1, see experimental for details) shows that the characteristic ratio is essentially 1:1 and that *m/z* 38.5 and 39.5 are the most intense peaks in the cluster at *m/z* 36−41; in contrast, for $\mathbf{2}^{\bullet+}$ the ratio is 2.5:1 and doubly charged ions are really barely visible in the shoulders of the *m/z* 39 and 40 peaks. More importantly, the CID mass spectrum of the *m/z* 79 ions generated by the metastable dissociation of picolinic acid molecular ions is the same as the spectrum of the ions which are generated by CO_2 loss in the ion source. Since the parent ions undoubtedly possess different internal energy distributions in the two cases one would expect a variation in the proportion of fragment ions produced if dissociation yielded a mixture of isomers rather than a single species. Thus, we conclude that dissociative ionization of 2-picolinic acid gives preferentially if not exclusively $\mathbf{1}^{\bullet+}$ rather than a mixture of the two isomers. It is clear though from the similarity of the CID mass spectra of the two isomers that large differences are not necessarily to be expected in the NR mass spectra of $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$.

Indeed, despite the fact that the disparities between the two NR mass spectra are greater than for the corresponding CID mass spectra, the key *m/z* 26:28 ratio is not isomer distinguishing. In fact, using cyclopropane as a neutralization agent the NR ratio is 4:1 for $\mathbf{2}^{\bullet+}$ and even larger, 5.5:1, for $\mathbf{1}^{\bullet+}$. Nevertheless, both spectra do contain peaks at *m/z* 79, corresponding to reionized $C_5H_5N^{\bullet+}$ ions. Furthermore, the use of organic neutralization agents with low ionization energies, which more closely match the recombination energies of the carbenes, are more likely to give near resonant electron transfer, and it was noted that the use of *N*,*N*-dimethylaniline as the reducing agent led to considerably less fragmentation in the NR mass spectrum of $\mathbf{1}^{\bullet+}$ (*m/z* 26:28 ratio = 2.7:1), which thus bears a greater resemblance to the CID mass spectrum. It is still not possible though to assign the structure of the stable neutral species at this juncture. Similar problems plague other systems,[19,20,42] and it has been shown previously that neutral identification may still be feasible by selectively analyzing the ions recovered after the NR process.[18] This NR/CID type of multiple collision experiment is demanding in terms of sensitivity but extremely revealing as will be demonstrated. It should be mentioned that NR, but not NR/CID experiments, have been used to probe the structure of the C_5H_5N neutral produced in an interesting nitrogen atom translocation reaction of $(C_5H_5)_2Fe_2NO^+$, and it was suggested that pyridine was the molecule produced.[43] Although it would seem now that the structure of the product cannot be unequivocally assigned on the basis of these results, thermodynamic considerations (vide infra) still favor the earlier suggestion.[43]

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Table 1. CID and NR Mass Spectra of $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$

	$\mathbf{1}^{\bullet+}$			$\mathbf{2}^{\bullet+}$		
(m/z)	CID [O_2][a]	NR [Δ,O_2][b]	NR [Me_2NPh,O_2][c]	CID [O_2][a]	NR [Δ,O_2][b]	CID [He][d]
79		24	49		90	
78	14	12	12	11	13	25
77	2	6	3	1	3	5
76	3	7	4	2	4	5
75	2	7	4	2	4	2
53	11	17	9	6	6	7
52	100	100	100	100	100	100
51	45	89	64	44	98	65
50	28	84	47	25	61	51
49	7	34	15	6	20	10
48	2	8	4	2	6	2
40	5	11	6	3	9	4
39.5	12			5		
39	11	25	17	11	24	15
38.5	12					
38	11	41	24	10	35	16
37	9	53	27	8	37	11
36	3	27	12	3	17	2
28	9	12	10	4	11	7
27	6	96	24	4	47	6
26	9	68	27	10	44	20
25	4	36	13	3	20	3
24	2	19	6	2	9	1
13		6	2		4	
12	1	10	3	<1	5	<1

[a] CID [O_2] indicates collision induced dissociation with oxygen performed between B and E_1 on 10 kV source generated ions. [b] NR [Δ,O_2] indicates neutralization with cyclopropane and reionization with oxygen performed between B and E_1 on 10 kV source generated ions. [c] NR [Me_2NPh,O_2] indicates neutralization with *N*,*N*-dimethylaniline and reionization with oxygen performed between B and E_1 on 10 kV source generated ions. [d] CID [He] of 10 kV source generated ions occurred in the third field free region between E_1 and E_2. The resolution of E_1 and E_2 are different so direct comparison is most appropriate to spectra in Figure 1.

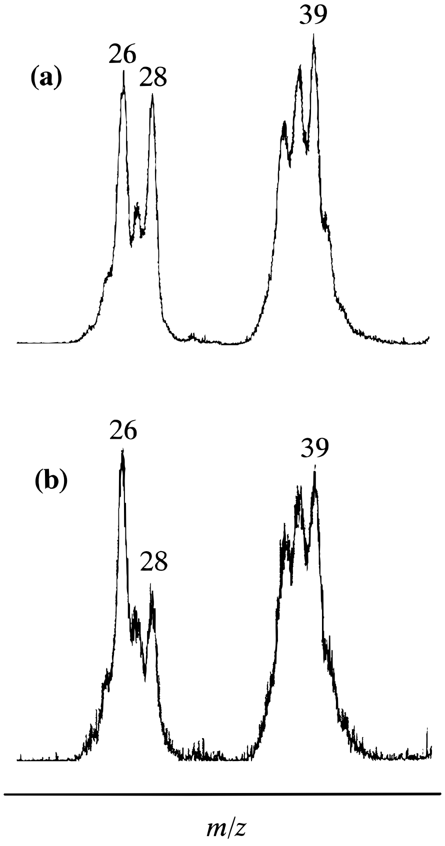

Figure 1. NR/CID (see text) mass spectrum of the m/z 79 ions generated from (a) ionized 2-picolinic acid and (b) ionized pyridine.

Partial NR/CID mass spectra of $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ are shown in Figure 1 (parts a and b, respectively). The former spectrum represents the m/z 79 ions obtained from picolinic acid, but it should be noted that the NR/CID mass spectrum of the m/z 79 ions generated from methyl picolinate was essentially superimposable upon it. A comparison of the different NR/CID mass spectra reveals several things. First, two ions ($\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$) are once again discernable by CID following the neutralization−reionization events. Second, the NR/CID mass spectrum from each isomer is extremely similar to the corresponding CID mass spectrum (not shown). So, in spite of the common dissociation channels which are accessed by $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$, they are sufficiently different from one another to permit isomer identification. That this is undoubtedly the case can be seen from a comparison of the NR/CID mass spectrum (Figure 2a) of the labeled ion D_1-$\mathbf{1}^{\bullet+}$ with its CID mass spectrum (Figure 2b), which reveals the two to be nearly identical. These results demonstrate that the structural integrity of the species are maintained throughout the NR process, and, furthermore, the original ion fluxes were constituted of only a single $C_5H_5N^{\bullet+}$ isomer. If this were not the case, since the two isomers are expected to have different efficiencies at each collision step, an enrichment of one relative to the other would take place, and the resulting NR/CID spectra would be intermediate in appearance between the CID spectra of the two isomers. The slight difference in the relative intensity of m/z 40 for the labeled ions is thus attributed to a small amount of post-collisional isomerization of the ions, which can occur below the threshold for dissociation. As indicated below by our calculations, neutral tautomerization is in principle also possible since despite its substantial height the barrier is low enough to be surmounted without dissociation.[44] However, the evidence leads us to the conclusion that neutral **1** is a stable species, which does not easily interconvert with **2** although this tautomerization undoubtedly occurs for some of the excited species.

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[44] BDE (C−H) = 134 kcal/mol according to data: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

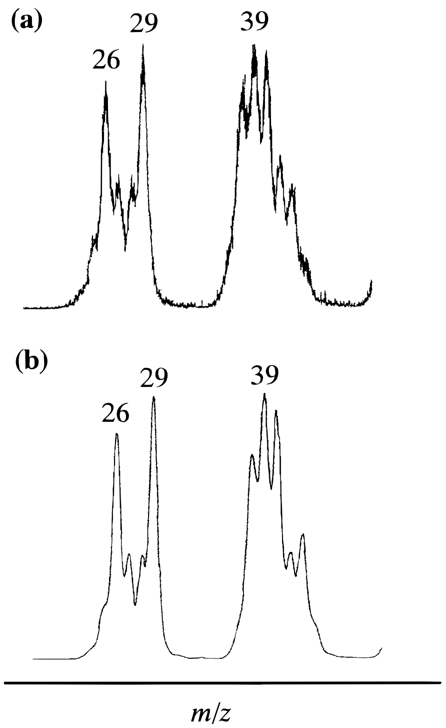

Figure 2. (a) NR/CID (see text) mass spectrum and (b) CID mass spectrum of the $C_5H_4DN^{\bullet+}$ ions (*m/z* 80) generated from ionized 2-(D_3-methyl) picolinate acid.

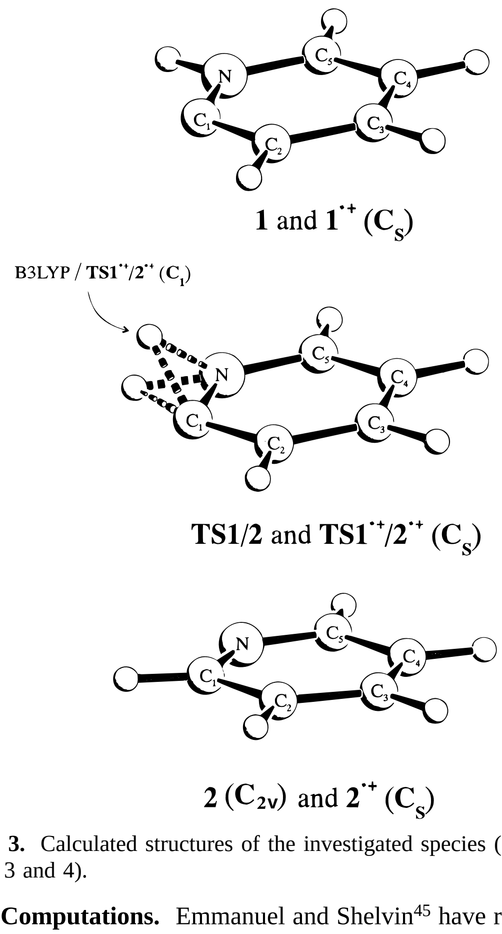

Figure 3. Calculated structures of the investigated species (see also Tables 3 and 4).

B. Computations. Emmanuel and Shelvin[45] have recently considered some of the C_5H_5N potential energy surface to explain the production of pyridine in reactions of atomic carbon with pyrrole. Of course, pyridine and its radical cation, i.e., **2** and **2**$^{\bullet+}$, are already well-known to computational chemists,[46] but by contrast the isomer **1** and its ionized counterpart **1**$^{\bullet+}$ are virtually unknown.[27] Of the latter two, there are reports only concerning the neutral species **1**, and to our knowledge there have not been any previous studies of the transition states for interconversion of either the neutral or ionic species. Since one way of looking at **1** is in terms of a carbene, special care has to be taken to adequately describe the electronic structure of this species, and single determinant based methods such as MP2 might not be sufficient.[47] We therefore performed CASSCF-MP2 calculations on the neutral and ionic minima species in which degeneracy effects are properly taken care of in order to calibrate the accuracy of the MP2 and B3LYP approaches.[48] However, from the results presented below and the analysis of the CASSCF wave function we can safely conclude that none of the minima considered requires a multireference treatment. For the open shell species the CASSCF wave function has the further advantage of being a spin eigenfunction, whereas the unrestricted reference wave functions do show significant spin contaminations in the MP2 calculations. The B3LYP approach suffers much less from this problem.[49] The computed total and relative energies together with the $\langle S^2 \rangle$ expectation values in the case of the open shell systems are summarized in Table 2.

All four species, pyridine-2-ylid (**1**), pyridine (**2**), and their respective radical cations **1**$^{\bullet+}$ and **2**$^{\bullet+}$, are identified as genuine minima characterized by a positive definite Hessian matrix at the MP2 and B3LYP levels of theory. Neutral pyridine is, of course, much more stable than the isomeric form **1**, the energy difference amounts to 50.2 and 46.8 kcal/mol at MP2/6-31G** and B3LYP/6-31G**, respectively. At the CASSCF-MP2 level, employing the harmonic frequencies as determined at the MP2 level for the ZPE corrections, we obtain 49.0 kcal/mol for this quantity. The ground state of **1** is undoubtedly a $^1A'$ singlet, the lowest lying ($^3A''$) triplet state is theoretically predicted to be 44.2 and 35.6 kcal/mol higher in energy at MP2 and B3LYP, respectively. It should be noted that the MP2 wave function for the $^3A''$ state is severely spin contaminated ($\langle S^2 \rangle = 2.395$) which renders the corresponding triplet energy a bit questionable. Indeed, the CASSCF-MP2 singlet–triplet gap is 36.4 kcal/mol, almost identical to the B3LYP result, but clearly smaller than the result obtained at the MP2 level. These computed energy differences are in line with the singlet–triplet gaps found for other amino carbenes, i.e., 50 kcal/mol for amino carbene and 78 kcal/mol for imidazol-2-ylidene.[14] For the cations, the two isomers **1**$^{\bullet+}$ ($^2A'$) and **2**$^{\bullet+}$ ($^2A_1$) are much closer in energy. At MP2 and CASSCF-MP2, the pyridine radical cation is less stable than **1**$^{\bullet+}$ by 5.5 and 7.4 kcal/mol, while using our B3LYP results put **1**$^{\bullet+}$ just 1.1 kcal/mol above **2**$^{\bullet+}$ instead. It should be noted that the latter stability order results only after inclusion of the ZPE, the uncorrected total energies slightly favor **1**$^{\bullet+}$ (by less than 1 kcal/mol). The relevant optimized geometry parameters of **1**, **2**, **1**$^{\bullet+}$, and **2**$^{\bullet+}$ are given in Table 3 along with

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[45] Emmanuel, C. J.; Shelvin, P. B. *J. Am. Chem. Soc.* **1994**, *116*, 5991.

[46] (a) Tantardini, G. F.; Simonetta, M. *Int. J. Quant. Chem.* **1981**, *20*, 705. (b) Walker, I. C.; Palmer, M. H.; Hopkirk, A. *Chem. Phys.* **1990**, *141*, 365. (c) Nakano, H.; Nakajima, T.; Obara, S. *Chem. Phys. Lett.* **1991**, *177*, 458. (d) Foresman, J. B.; Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *J. Phys. Chem.* **1992**, *96*, 135. (e) Fulscher, M. P.; Andersson, K.; Roos, B. O. *J. Phys. Chem.* **1992**, *96*, 9204.

[47] See, e.g.; Liebman, J. F.; Simons, J. In *Molecular Structure and Energetics*, Liebman, J. F., Greenberg, A., Eds., VCH: Deerfield Beach, FL, 1986; Vol. I.

[48] Due to the loss of symmetry in the saddle points and the importance of the C–H and N–H bonds being formed or broken in the rearrangement processes, no straightforward selection of an active space, which is consistent with the description of the minima and at the time still manageable computationally, was possible. We therefore limited our CASSCF/MP2 calculations to the minima.

[49] Baker, J.; Scheiner, A.; Andzelm, A. *Chem. Phys. Lett.* **1993**, *216*, 380.

Table 2. Calculated Energies for Selected C_5H_5N Neutrals, Radical Cations, and Transition States, Employing the 6-31G** Basis Set[a,b]

species	MP2	$\langle S^2\rangle$	ZPE	E_{rel}	B3LYP	$\langle S^2\rangle$	ZPE	E_{rel}	CASSCF-MP2	E_{rel}[d]
$^{1}\mathbf{1}$[c]	−247.44196	0.0	54.5	50.2	−248.21778	0.0	55.6	46.8	−247.40445	49.0
$^{3}\mathbf{1}$[c]	−247.36936	2.395	53.1	94.5	−248.15738	2.037	53.3	82.4	−247.34432	85.4
2	−247.52180	0.0	54.4	0.0	−248.29260	0.0	55.8	0.0	−247.48246	0.0
TS1/2	−247.37542	0.0	50.3	87.9	−248.14978	0.0	51.3	85.1		
$\mathbf{1}^{\bullet+}$	−247.19730	0.956	58.0	207.1	−247.96762	0.758	56.1	204.2	−247.15554	208.6
$\mathbf{2}^{\bullet+}$	−247.18665	1.096	56.8	212.6	−247.96637	0.757	54.2	203.1	−247.14187	216.0
$\mathbf{TS1}^{\bullet+}/\mathbf{2}^{\bullet+}$	−247.09296	0.876	54.5	269.2	−247.86935	0.760	51.4	261.2		

[a] Total energies in Hartree, relative and zero-point energies in kcal/mol. Relative energies include the ZPE. [b] ZPE determined at MP2 scaled by 0.9646.[37] [c] The superscript designates the state of the ylide, i.e., singlet or triplet. [d] ZPE corrections taken from MP2 data.

Table 3. Selected Calculated Geometric Parameters for **1**, $\mathbf{1}^{\bullet+}$, **2**, and $\mathbf{2}^{\bullet+}$ at Various Levels of Theory and Employing the 6-31G** Basis Set[a]

	1 (C_s)			$\mathbf{1}^{\bullet+}$ (C_s)		
parameter	B3LYP	MP2	CASSCF	B3LYP	MP2	CASSCF
$r(C_1N)$	1.374	1.374	1.348	1.329	1.317	1.323
$r(C_5N)$	1.367	1.364	1.371	1.365	1.362	1.350
$r(C_1C_2)$	1.433	1.429	1.448	1.370	1.340	1.377
$r(C_5C_4)$	1.371	1.376	1.360	1.381	1.343	1.382
$r(C_2C_3)$	1.384	1.390	1.372	1.404	1.378	1.397
$r(C_4C_3)$	1.411	1.403	1.422	1.403	1.391	1.402
$a(NC_1C_2)$	109.8	109.1	110.6	124.6	126.1	123.7
$a(NC_5C_4)$	119.0	118.6	119.4	118.6	119.7	118.8
$a(C_1C_2C_3)$	124.6	125.2	124.1	115.4	114.1	116.0
$a(C_5C_4C_3)$	117.6	117.9	117.6	119.9	118.7	119.7

	2 (C_{2v})				$\mathbf{2}^{\bullet+}$ (C_s)		
parameter	B3LYP	MP2	CASSCF	exp	B3LYP	MP2	CASSCF
$r(C_1N)$	1.345	1.321	1.332	1.338	1.313	1.302	1.321
$r(C_1C_2)$	1.395	1.385	1.395	1.394	1.406	1.363	1.394
$r(C_2C_3)$	1.394	1.384	1.393	1.392	1.397	1.374	1.399
$a(CNC)$	116.7	117.7	117.6	116.9	132.5	131.3	132.3
$a(NC_1C_2)$	123.8	123.6	123.5	123.8	114.3	115.0	114.2
$a(C_2C_3C_4)$	118.7	118.7	118.6	118.5	121.1	121.8	121.0

[a] Bond lengths in Å, angles in deg.

Table 4. Selected Calculated Geometric Parameters for **TS1/2** and $\mathbf{TS1}^{\bullet+}/\mathbf{2}^{\bullet+}$ at the B3LYP and MP2 Levels of Theory Employing the 6-31G** Basis Set[a]

	TS1/2		$\mathbf{TS1}^{\bullet+}/\mathbf{2}^{\bullet+}$	
parameter	B3LYP	MP2	B3LYP	MP2
$r(C_1N)$	1.387	1.391	1.305	1.265
$r(C_5N)$	1.350	1.353	1.368	1.356
$r(C_1C_2)$	1.410	1.412	1.395	1.352
$r(C_5C_4)$	1.384	1.384	1.386	1.333
$r(C_2C_3)$	1.391	1.392	1.395	1.366
$r(C_4C_3)$	1.407	1.404	1.415	1.405
$r(NH_1)$	1.175	1.164	1.300	1.254
$r(C_1H_1)$	1.360	1.365	1.309	1.360
$a(C_1NC_5)$	125.7	126.7	121.5	125.4
$a(NC_1C_2)$	116.0	115.0	127.0	127.1
$a(NC_5C_4)$	118.4	117.5	115.7	112.8
$a(C_1C_2C_3)$	119.8	120.3	112.1	109.1
$a(C_5C_4C_3)$	121.2	119.6	121.2	120.8
$a(C_1NH_1)$	63.5	64.0	60.3	65.3
$a(NC_1H_1)$	50.7	49.9	59.6	56.9
$d(H_1C_1NC_5)$	180.0	179.7	129.8	180.0

[a] Bond lengths in Å, angles in deg.

the experimental data for neutral pyridine. Overall, all three methods (MP2, CASSCF, B3LYP) yield very similar equilibrium geometries; however, compared to the experimental structure of pyridine, the B3LYP and CASSCF procedures are very similar to each other and slightly outperform the MP2 approach. In spite of the constraint of the ring system, the singlet and the triplet of **1** have slightly different geometries. In particular the NC_1C_2 bond angle is larger in the triplet as compared to the singlet (ca. 115° versus ca. 110°). The NC_1C_2 angle in the radical cation $\mathbf{1}^{\bullet+}$ (124.6° (B3LYP), 126.1° (MP2), and 123.7° (CASSCF)) is more similar to that of the triplet, which is consistent with the HOMO of the singlet being largely localized at the dicoordinate carbon atom. Compared to pyridine,[50] there is thus a noticeable widening of this angle.

The structures of the saddle point for the intramolecular interconversion of the two isomeric forms are very similar at the B3LYP and MP2 levels of theory for the neutral rearrangement **TS1/2**. However, whereas the B3LYP structure is strictly planar and keeps C_s symmetry, at the MP2 level this saddle point adopts a C_1 symmetric structure in which the hydrogen atom migrates very slightly (0.3°) above the plane of the ring (Table 4). However, the deviation from C_s symmetry is so small that also at MP2 **TS1/2** should certainly be looked at as *de facto* planar. The two methods also yield very similar barrier heights. Coming from **1** the 1,2-hydrogen shift via **TS1/2** requires just under 40 kcal/mol, 38.4 or 37.7 kcal/mol according to B3LYP or MP2, respectively. Interestingly, for the ionic transition state $\mathbf{TS1}^{\bullet+}/\mathbf{2}^{\bullet+}$ the saddle point geometries turn out to be strongly method dependent as documented in Table 4. B3LYP predicts a nonplanar, C_1 symmetric structure (dihedral angle $H_1-C_1-N-C_5 = 129.8°$), see Table 4. Using the MP2 scheme instead yields a planar, C_s symmetric transition structure. We note in passing that the structure of $\mathbf{TS1}^{\bullet+}/\mathbf{2}^{\bullet+}$ optimized at the Hartree–Fock level with a 6-31G** basis set very closely resembles the nonplanar geometry obtained at B3LYP. Significant activation barriers, which again is similar for both methods, of 57.0 and 56.6 kcal/mol at B3LYP and MP2, respectively, with respect to the least stable $C_5H_5N^{\bullet+}$ isomer, are connected with this saddle point. The minimum energy needed for fragmentation of $\mathbf{2}^{\bullet+}$ (which undoubtedly represents the lowest energy dissociation necessary for $\mathbf{1}^{\bullet+}$ as well) has been experimentally determined as 95.6 kcal/mol,[51] so it should be possible for some internally excited ions to communicate below the dissociation threshold. This is consistent with the experimental observation that metastable ions $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ freely interconvert giving identical MI spectra, whereas most of the ions sampled in the CID and NR/CID experiments reside below the isomerization barrier until activated by the collision, whereupon isomerization is able to occur for some species prior to their dissociation. Nevertheless, the species all have fairly deep energy wells, which should minimize the likelihood of isomerization in NRMS experiments, consistent with the observation of differentiable NR/CID mass spectra for the isomers.

C. Thermochemistry. A combination of experimental and theoretical approaches have been used to evaluate thermochemical data for species pertinent to the present study. It is not possible to obtain a reliable heat of formation for $\mathbf{1}^{\bullet+}$ using picolinic acid since the peak corresponding to the dissociation of metastable molecular ions is dish-shaped, which indicates that there is a substantial reverse energy term associated with

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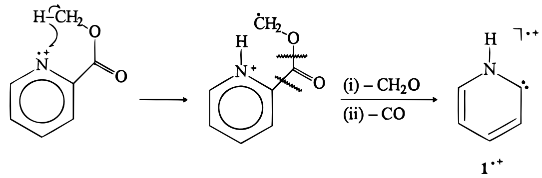
(50) Spitzner, D. In *Houben-Weyl*; Band E7b, Teil 2, Georg Thieme Verlag: Stuttgart, Germany, 1992; p 286.

(51) Lifshitz, C. *J. Phys. Chem.* **1982**, *86*, 606.

the reaction. Fortunately, this is not the case for methyl picolinate, which shows narrow Gaussian shaped peaks for the successive losses of CH_2O and CO. Therefore, we have used the method of Burgers and Holmes[52] to measure the appearance energy (AE) of the $C_5H_5N^{\bullet+}$ ion produced from metastable methyl picolinate molecular ions (eq 1).



$\mathbf{1}^{\bullet+}$ (1)

The heat of formation of the precursor molecule, −57 kcal/mol, was estimated from the known ΔH_f of 2-methylpyridine (24 kcal/mol) and the difference between toluene ($\Delta H_f = 12$ kcal/mol) and methyl benzoate ($\Delta H_f = -68$ kcal/mol) under the assumption that there is no unusual effect upon substitution of $-CH_3$ by $-CO_2CH_3$ adjacent to the hetero atom. This value and the measured AE of 10.14 eV, when combined with the known values for CH_2O (−26 kcal/mol) and CO (−26 kcal/mol), lead to $\Delta H_f(\mathbf{1}^{\bullet+}) = 237 \pm 5$ kcal/mol.

It is also possible to evaluate the $\Delta H_f(\mathbf{1}^{\bullet+})$ from the computational data with reference to the heat of formation of pyridine, either from the differences between the two ions and the ionization energy (IE) of **2** or from the calculated difference between the two neutrals and IE(**1**). Using the former route and $\Delta H_f(\mathbf{2}^{\bullet+}) = 246$ kcal/mol, from the experimental $\Delta H_f(\mathbf{2}) = 33$ kcal/mol and the well established IE(**2**) = 9.25 eV, together with the calculated energy difference between $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$, 5.5 (MP2) and 7.4 kcal/mol (CASSCF-MP2), leads to $\Delta H_f(\mathbf{1}^{\bullet+}) = 240$ and 239 kcal/mol, respectively, in excellent agreement with experiment. Employing the B3LYP difference between $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ (1 kcal/mol in favor of $\mathbf{2}^{\bullet+}$) leads to a slightly less satisfactory result of $\Delta H_f(\mathbf{1}^{\bullet+}) = 247$ kcal/mol. Using MP2 or CASSCF-MP2 the calculated adiabatic IEs(**2**) = 9.23 and 9.38 eV are close to the experimental value. On the other hand, at the B3LYP level of theory the IE(**2**) is slightly underestimated, 8.81 eV. However, the adiabatic IE of **1** is essentially the same, i.e., 6.81, 6.93, or 6.83 eV, for the three methods, MP2, CASSCF-MP2 and B3LYP, respectively. Since this is the case and the enthalpy difference between **1** and **2** is also quite close for these methods, 50, 49, or 47 kcal/mol, a consistent value for $\Delta H_f(\mathbf{1}^{\bullet+}) = 237-242$ kcal/mol can be derived from these data. The consistency between these methods and the similarity with the experimentally measured value gives us confidence in the proposed value $\Delta H_f(\mathbf{1}^{\bullet+}) = 237 \pm 5$ kcal/mol.

The energy difference between the two neutrals can be combined with $\Delta H_f(C_5H_5NH^+) = 178$ kcal/mol, determined from the proton affinity of pyridine,[53] PA(**2**) = 221 kcal/mol, to yield an estimate for PA(**1**) ≅ 270 kcal/mol.[54] This value is even higher than the one predicted for the imidazoline carbene, and thus would be one of the largest for a simple organic molecule.[13,53]

Finally, the high barriers to isomerization indicated by the computational and experimental results point to the possibility of directly observing **1** in the condensed phase under appropriate conditions, e.g., by low temperature matrix isolation.

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(52) Burgers, P. C.; Holmes, J. L. *Org. Mass Spectrom.* **1982**, *17*, 123.

(53) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

(54) A purely calculated PA needs to be corrected for ZPE and thermodynamic contributions (entropy). Dixon, D. A.; Lias, S. G. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: Deerfield Beach, FL, 1987; Vol. 2, Chapter 7, p 269.