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A Journey from Thermally-Tunable Synthesis to Spectroscopy of Phenylmethanimine in Gas Phase and Solution

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Abstract

Phenylmethanimine is an aromatic imine with a twofold relevance in chemistry: organic synthesis and astrochemistry. To tackle both aspects, a multidisciplinary approach has been exploited and a new, easily accessible synthetic approach to generate stable imine-intermediates in the gas phase and in solution has been introduced. The combination of this formation 6 pathway - based on the thermal decomposition of hydrobenzamide - with a state-of-the-art computational characterization of phenylmethanimine 8 laid the foundation for its first laboratory observation by means of rotational electric resonance spectroscopy. Both E and Z isomers have been 10 accurately characterized, thus providing a reliable basis to guide future as-11 tronomical observations. A further characterization has been carried out 12 by nuclear magnetic resonance spectroscopy, showing the feasibility of this 13 synthetic approach in solution. The temperature dependence as well as 14 possible mechanisms of the thermolysis process have been examined. 15

¹⁶ 1 Introduction

¹⁷ In the last few decades, astrochemistry –the research field focused on the chem-¹⁸ ical composition and evolution of ordinary matter in space– has flourished dy-¹⁹ namically: after being born as a niche sector it grew up into a field of broad

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interest. Its birth is relatively recent because, for many years, the interstellar 20 medium (ISM) -the space between star systems in a galaxy- has been con-21 sidered too hostile to bear any chemical complexity. However, with the rise of 22 radioastronomy (in the 1960s), it became evident that the ISM harbors a diverse 23 collection of interesting polyatomic (both organic and inorganic) molecules.^[1,2] 24 Since then, a large number of molecular species has been detected.^[3] Among 25 them, those having a prebiotic character are of particular interest because of 26 their key role in several mechanisms leading to the emergency of life. Imines 27 belong to this category. 28

While their astrobiological relevance has not yet unambiguously proven, 29 imines are known to play major roles in many chemical processes. They have 30 been recognized as crucial intermediates in organic synthesis, due to their exten-31 sive use in the preparation of N-containing compounds,^[4] and as naturally or 32 biologically active molecules.^[5] Because of peculiar and extreme conditions, the 33 chemical reactivity in space is very different from the terrestrial counterpart, 34 and unstable species (even ions and radicals) can survive long. As a conse-35 quence, reactive species such as some N-H imines, whose isolation is difficult on 36 Earth, can be observed in the ISM, ^[6-10] with the prerequisite of a successful 37 laboratory spectroscopy characterization. With the chemistry in the ISM being 38 new and intriguing, severe difficulties arise when interstellar molecules are to be 39 produced by "terrestrial" organic procedures for their characterization, e.g. by 40 molecular spectroscopy. Indeed, the instability of these species often requires 41 that they are directly generated inside the spectrometer using harsh conditions 42 and rather unpredictable techniques such as pyrolysis or electric discharge. We 43 have tried to reconcile these difficulties by developing a different and easier syn-44 thetic route, the thermally tunable formation of imines, which has been tested 45 both in the gas phase and in solution. 46

The subject of this work is the case study of phenylmethanimine (PMI), 47 which is a non-standard reactive molecule of potential astrochemical relevance. 48 Due to the large amount of hydrogen (in the form of H, H₂, and also H^+/H_3^+) 49 available in the ISM, hydrogenation is an efficient process^[11] and leads to the 50 formation of saturated or partially saturated molecules.^[12] On this ground, hy-51 drogenation of benzonitrile (BN) in the ISM can yield PMI, an interesting imine 52 in terms of chemical complexity and molecular evolution. This gained attention 53 because of the recent detection of BN in the cold-core Taurus Molecular Cloud 54 1 (TMC-1), which provided the unequivocal proof of the presence of benzene in 55 that cold environment, and -more generally- in the ISM.^[13] In turn, benzene 56 is the building block of polycyclic aromatic hydrocarbons (PAHs), which are 57 recognized (but spectroscopically not proven) to be important constituents of 58 small dust grains in interstellar clouds and are believed to play a key role in 59 the chemical evolution in space from both a catalytic and protective point of 60 view. [14] 61

Despite its appeal as a good approach for imine synthesis in ISM, on Earth, nitrile reduction using molecular hydrogen usually requires catalytic conditions which are not compatible with a single hydrogenation process. Catalytic processes directly lead to the saturated derivative, i.e. the corresponding amine,

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or to a mixture of primary-, secondary- and even tertiary-amines via reaction 66 of the N-H imine intermediates.^[15,16] This is due to the high reactivity of the 67 imine intermediate.^[17–21] The N-H imine derivatives of aliphatic or aromatic 68 aldehydes are known to be much less stable, and only in a few cases they have 69 been successfully isolated or characterized. ^[22,23] Indeed, the literature is rich of 70 examples supporting the instability and reactivity of these imines. The chem-71 ical labile nature of N-H imines, and the difficulties related to their isolation, 72 resulted in the employment of imines possessing various substituents on the 73 nitrogen atom (N-substituted imines). Therefore, the activating or protecting 74 groups introduced on the nitrogen atom need to be removed after the synthetic 75 endeavor. Based on the concept of atom economy, N-unsubstituted imines would 76 be ideal, since deprotection steps, to obtain the final products, are not required. 77 Unfortunately, unlike N-substituted imines, the approaches to N-unsubstituted 78 imines are limited to (and, in many cases, were proposed as) unstable, not char-79 acterized intermediates.^[24] The direct reaction with ammonia and aldehydes is 80 not a suitable synthetic procedure for such imines. N-H imines can be accessed 81 by the controlled hydrolysis of N-metalloimines or silvlimines.^[25] Another sim-82 ple access to N-H imines involves available azides precursors with the removal of 83 N₂ and subsequent migration of hydrogen, under catalytic conditions.^[26] Nev-84 ertheless, all these approaches are impracticable in order to generate N-H imines 85 for rotational spectroscopy investigations in gas phase. Indeed, such context in-86 creased the relevance of a thermally tunable approach from a simple precursor 87 for the generation of N-H imines and their spectroscopic investigation. Such 88 approaches avoid critical issues such as: (i) demanding experimental setups, i.e. 89 subtle control of reaction conditions; (ii) trapping procedures leading to imine 90 complexes; (iii) use of transition metal catalysts; (iv) unfeasible interface with 91 spectroscopic techniques. 92

The latter aspect is of particular interest to our investigation since, in order 93 to set up and validate our synthetic route, high-resolution spectroscopic tech-94 niques offer the highest specificity: rotational electric resonance (RER) spec-95 troscopy in the gas phase and nuclear magnetic resonance (NMR) spectroscopy 96 in solution. Since our strategy is based on two key points, namely (i) the use of 97 stable and affordable organic precursors and (ii) the generation of the unstable 98 and reactive imines through simple conditions, it provides a suitable way to 99 produce imines directly inside the spectrometer. 100

In this manuscript, we report a full account of our successful endeavor, which has led –for the first time– to a complete and accurate spectroscopic characterization of PMI using RER, which is prerequisite for its identification in the ISM by means of radioastronomy. It required a multidisciplinary effort combining organic synthesis and molecular spectroscopy, the latter supported and guided by computational chemistry.

¹⁰⁷ 2 Results and discussion

Spectroscopic characterization of PMI. To guide RER experiments, a 108 state-of-the-art quantum-chemical (QC) characterization has been performed. 109 Using the density functional theory (DFT, see supporting information, SI, for 110 details), a preliminary scan of the potential energy surface has been carried 111 out, which located two isomers (E and Z, referring to the relative position of 112 the phenyl group with respect to the imine hydrogen, see Figure 1). Subse-113 quently, an accurate structural determination has been obtained by resorting to 114 the so-called "cheap" composite scheme^[27] (hereafter denoted as ChS), whose 115 denomination refers to the limited computational cost in spite of its accuracy. 116 The ChS approach is expected to provide results with an accuracy of about 117 0.001-0.002 Å for bonds and 0.1-0.2° for angles.^[27] This approach has also been 118 used to derive accurate electronic energies, which are given in Figure 1. While 119 structural parameters and a detailed description of the ChS model are pro-120 vided in the SI, this figure points out that the E isomer is about $6 \,\mathrm{kJ}\,\mathrm{mol}^{-1}$ 121 more stable than the Z species. TS_{E-Z} has a quasi-linear C-N-H geome-122 try, the isomerization process occurring in the molecular plane, similarly to 123 what already observed for other imines such as ethanimine (ETI)^[28] and C-124 cyanomethanimine (CCMI).^[29] Although different computational schemes have 125 been applied, a qualitative comparison between the relative energies is possi-126 ble. A smaller energy difference between the two isomers was obtained for ETI 127 and CCMI $(2.8 \text{ kJ mol}^{-1} \text{ and } 2.0 \text{ kJ mol}^{-1}, \text{ respectively}^{[28,29]})$, while a similar 128 isomerization barrier was found (about 116 kJ mol^{-1} for ETI, $^{[28]} \sim 111 \text{ kJ mol}^{-1}$ 129



Isomerization coordinate

Figure 1: Stationary points of PMI, relative electronic energies at the ChS level. Values within parentheses are augmented by harmonic B2PLYP zeropoint energy corrections.

¹³⁰ for CCMI, ^[29] and about 112 kJ mol^{-1} for PMI).

Equilibrium rotational constants have been straightforwardly derived from 131 the ChS equilibrium structure, while the required vibrational corrections have 132 been evaluated from DFT anharmonic force-field calculations (thereby using 133 B3LYP,^[30,31] see SI for details). First-order properties, such as dipole moment 134 components and nuclear quadrupole coupling constants, have been computed 135 using, in the framework of DFT, the double-hybrid B2PLYP functional^[32] (see 136 SI for details). This level of theory has also been employed for deriving cen-137 trifugal distortion constants. 138

The gas-phase characterization of PMI has been performed in the 3-26 GHz 139 range, using the COBRA-type (Coaxially Aligned Beam Resonator Arrange-140 ment) Fourier Transform Microwave Spectrometer (FTMW), described in de-141 tails elsewhere.^[33] A nozzle valve, filled with hydrobenzamide (HBA) and heated 142 to 85 °C, was used to vaporize it and, at the same time, to thermally-decompose 143 it, thus producing PMI in the gas phase. HBA was synthesized, following the 144 procedure described in literature, ^[17,34–36] by condensation of benzaldehyde and 145 ammonium hydroxide solution and obtained as white solid, with its identity and 146 purity being confirmed by NMR analysis (see the SI for details). 147

Given the high accuracy of the QC calculations performed (the relevant spec-148 troscopic parameters are collected in Table 1), the computational prediction of 149 the rotational spectrum was expected to match the accuracy [37] required for 150 an unequivocal identification of the E and Z isomers of phenylmethanimine in 151 the gas phase. Indeed, it was straightforward to successfully identify and as-152 sign more than one hundred transition frequencies for both PMI isomers. Their 153 unique pattern (hyperfine structure), due to quadrupole coupling splitting orig-154 inated by the presence of ¹⁴N nucleus (I = 1), is shown in Figure 2 for both 155



Figure 2: The $4_{1,4} \leftarrow 3_{1,3}$ transition of *E*-phenylmethanimine (top panel) and the $4_{0,4} \leftarrow 3_{0,3}$ transition of the *Z* isomer (bottom panel), denoting rotational transitions $J_{K_a,K_c} \leftarrow J'_{K'_a,K'_c}$. In both spectra, the reported quantum numbers refer to the nuclear quadrupole coupling scheme $F \leftarrow F'$, F = J + I and the line pairs becoming split by the Doppler effect are made evident.

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	E-phenylmethanimine		Z-phenylmethanimine	
	exp.	best theo.	exp.	best theo.
A	5217.29202(11)	5216.95	5200.81278(16)	5200.42
B	1565.283633(28)	1564.68	1548.969349(92)	1548.76
C	1204.540307(14)	1204.05	1194.842313(78)	1194.30
$D_J \times 10^5$	5.775(11)	5.57	5.643(35)	5.28
$D_K \times 10^4$	7.65(11)	7.07	7.06^{b}	7.06
$D_{JK} \times 10^4$	1.678(37)	1.81	1.445(47)	1.57
$d_1 \times 10^5$	-1.6941(55)	-1.63	-1.542(44)	-1.51
$d_2 \times 10^6$	-3.162(23)	-3.00	-2.68^{b}	-2.68
$1.5\chi_{aa}$	1.5271(14)	1.61	-5.8871(23)	-6.05
$0.25(\chi_{bb}-\chi_{cc})$	-1.70630(38)	-1.83	-0.4954(15)	-0.55
$ \mu_a $		0.77		3.09
$ \mu_b $		1.66		0.15
$ \mu_c $		0		0
# lines ^c	180		118	
$ m rms imes 10^3$	4.56		1.38	
$\sigma^{ m d}$	0.65		0.69	

Table 1: Comparison between experimental (exp.) ^a and calculated (best theo.)
spectroscopic parameters (expressed in MHz, dipole moment components are
given in debye).

^a S reduction, I^r representation. Standard errors are reported within parentheses.

^b Fixed at the corresponding computed value.

^c Distinct frequency lines.

^d Dimensionless quantities.

PMI isomers. Furthermore, we note that each rotational transition appears 156 as a doublet due to the Doppler effect arising from a supersonic jet expan-157 sion. For the most stable E-PMI, the spectral analysis has been extended in 158 the 83-100 GHz, thus allowing the improvement of the spectroscopic parame-159 ters, using a frequency-modulation millimeter-wave (FM-mmW) spectrometer 160 (see ref. 38 for a detailed description). In this experiment, a different pro-161 duction method of PMI has been employed, as reasoned below. Indeed, PMI 162 was produced by means of flash vacuum pyrolvsis (FVP)^[39,40] of a sample of 163 α -methylbenzylamine (890 °C). 164

The spectroscopic parameters derived from a weighted non-linear fit of the 165 observed transitions, performed using the Pickett's CALPGM suite of programs, ^[41] 166 are reported in Table 1. An excellent agreement between the computed and ex-167 perimental values can be noted, with an average error of 0.03% on the effective 168 rotational constants and a maximum discrepancy below 0.05%. Only small de-169 viations have also been found for the quartic centrifugal distortion and nuclear 170 quadrupole coupling constants. Since rotational and quadrupole coupling con-171 stants are strongly tied to the molecular structure, the very good agreement 172

gives further confidence in the reliability and accuracy of the computed geome-tries.

¹⁷⁵ While the full list of the rotational transitions included in the fit is given in ¹⁷⁶ the SI, we state here that the root mean square error (rms) is smaller than 5 kHz, ¹⁷⁷ with a standard deviation (σ) slightly below unity, i.e. achieving experimental ¹⁷⁸ accuracy.

Thermal decomposition of HBA. The successful generation and charac-179 terization of PMI in the gas phase raised questions about the mechanism of 180 its formation and the possible extension of the methodology to the condensed 181 phase (i.e. solution) and, more generally, to other N-unsubstituted imines (thus 182 avoiding more expensive and/or more chemically demanding procedures). For 183 this reason, the thermal behavior of HBA has been explored from room tem-184 perature to 100/110 °C, both in the gas phase by means of RER and in solution 185 by ¹H-NMR. 186

In particular, the $J_{K_a,K_b} = 5_{0,5} \leftarrow 4_{0,4}$ rotational transition of four molecular species, namely the BA, BN and the *E* and *Z* isomers of PMI, has been recorded with the COBRA-FTMW spectrometer. To provide a reliable comparison between the intensity of the transitions, the power of the microwave



Figure 3: Spectra of the $J_{K_a,K_b} = 5_{0,5} \leftarrow 4_{0,4}$ transition for the four molecular species investigated (PMI: phenylmethanimine; BA: benzaldehyde, BN: benzaldehyde). The huge abundance of BA in the gas phase leads to out-of-chart transitions at any temperature.

excitation pulse has been scaled according to the value of dipole moment com-191 ponent along the a-axis and a 2000 averaging signal acquisition has been chosen. 192 The recording has been started ten minutes after the temperature set up. The 193 recorded spectra (see Figure 3) reveal the presence of BA at all temperatures, 194 while clearly distinguishable signals of PMI isomers are observed only above 195 80 °C. BN lines appear at the same temperature. For both PMI isomers and 196 BN, it is noted that rising the temperature increases the intensity of the tran-197 sitions, thus improving the signal-to-noise ratio (S/N). Although not shown in 198 Figure 3, the 12321.0 MHz transition of the water dimer^[42] was observed for 199 each temperature increment. This confirms the steady presence of water in the 200 experimental apparatus, which very likely plays a key role in the investigated 201 hydrolytic process. 202

An important note on the relative populations of the two PMI isomers is 203 deserved. In principle, this information should be derivable from the spectra of 204 Figure 3: however, the E-PMI transition there reported lies very close to the 205 strong transition of BA, this clearly modifying the baseline of the E-PMI tran-206 sition. As a consequence, the signal-to-noise ratios of Z-PMI and E-PMI lines 207 cannot be compared, thus preventing the derivation of the relative populations. 208 We can only comment that, during the recording of the spectra, we noticed 209 that the intensities of both isomers were comparable. This is probably due to 210 a co-operation of population distribution and differences in the electric dipole 211 moment components. 212

As to the NMR characterization, according to the available literature data, 213 PMI shows two distinct sets (each with two doublets) of signals for the imino hy-214 drogen, with different coupling constants (J = 16 Hz for the E isomer, J = 25215 Hz for the Z one).^[26] In our analysis, the sample was heated to the desired 216 temperature and the ¹H-NMR spectrum was acquired after 10 minutes to avoid 217 thermalization processes during the acquisition (a complete account of the ex-218 periment is provided in the SI). The formation of both BA and E-PMI was ob-219 served as a consequence of the step-by-step temperature increasing from $25\,^{\circ}\mathrm{C}$ 220 to 110 °C (see Figure 4). However, no spectroscopic clues denoting the possi-221 ble formation of BN or Z-PMI were observed, even when the experiments were 222 conducted at higher temperature. As far as Z-PMI is concerned, however, our 223 experimental resolution did not allow for unequivocally excluding its presence. 224 This suggests that the two experiments (RER and NMR) are characterized by 225 either different hydrolytic mechanisms or the availability of additional pathways 226 in the case of gas-phase measurements. To confirm the absence of BN in solution 227 after thermal treatment of HBA, a trace amount of the former was added to the 228 NMR samples previously heated at 110 °C and the spectrum was again recorded. 229 The analysis revealed the presence of new signals (doublet at 7.68 ppm, over-230 lapping with a BA triplet: doublet at 7.63 ppm; triplet at 7.50 ppm, overlapping 231 with a HBA multiplet), due to the presence of BN and previously absent. Hence, 232 no BN is formed by hydrolysis of HBA in solution (see SI). This might suggest 233 that its generation occurs through pathways that rely on metallic catalytic sur-234 faces, such as fast dehydrogenation of PMI.^[43,44] Indeed, it has been proved that 235 the metal catalysis can take place in the nozzle head in the RER experiment,^[45] 236

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Figure 4: Top panel: NMR signals at different temperatures for HBA and its thermolysis products. Bottom panel: Temperature-dependence of the normalized integral values (residual solvent peak was fixed to 10) of the NMR signals. In both panels, red triangles refer to HBA CHN (8.63-8.60 ppm), cyan hexagons to aminal HBA (6.06-5.99 ppm), blue upside down triangles to PMI *ortho*-protons (7.77-7.76 ppm), green diamonds to BA *para*-proton (7.68 ppm), black squares to BA CHO (10.08-10.02 ppm) and grey circles to PMI CHN (8.70 ppm). The aminal HBA signal is not shown in the top panel for the sake of clarity.

9



Scheme 1: Proposed mechanism for HBA hydrolysis.

²³⁷ while this is not the case within the NMR tube.

Figure 4 shows the changes –upon heating– of the diagnostic NMR signals 238 (top) and the temperature-dependence of their normalized integral values with 239 the respective linear regressions (bottom). Such analysis was performed after 240 an arbitrary assignment to the integral value of the residual peak of 1.1.2.2-241 tetrachloroethane- D_2 (fixed to 10). The negative-slope traces correspond to the 242 starting material, i.e. HBA, while the positive-slope traces are attributable to 243 forming species. As expected, the signal relative to the two CHN protons of 244 HBA (red trace) decreases twice as fast as the single-proton aminal signal (cyan 245 246 trace).

Two signals (i.e. green and black traces) have almost superimposed trends 247 in terms of both slope and normalized integral values, thus suggesting that the 248 respective protons belong to the same species. Indeed, they are compatible 249 with the CHO and *para*-proton (triplet) of BA, respectively, thus featuring a 250 1:1 integration relationship. The other two signals (i.e. blue and gray traces) 251 feature a 2:1 integration relationship. In particular, the singlet at 8.70 ppm (gray 252 trace) is compatible with an iminic CHN proton, while the doublet at 7.77 ppm 253 (blue trace) is compatible with the iminic *ortho*-protons. Furthermore, the grey 254 trace has a slope which is similar to those observed for the aldehydic signals, 255 thus suggesting that the generation processes of the two species are somehow 256 interconnected. The fact that BA appears to be produced before PMI suggests 257 that the involved hydrolytic mechanism proceeds with the initial formation of 258 BA, followed by the formation of PMI starting from other transient species. 259

Here, we propose a putative hydrolytic pathway (Scheme 1) which is compatible with the aforementioned observations and with previously proposed mechanisms.^[46-48] As mentioned above, the additional pathway leading to the formation of BN starting from PMI during the measurements in the microwave range
is supposed to be a dehydrogenation.

In our opinion, the following key points need to be analysed to explain the proposed mechanism: (i) the role of water; (ii) the role of the metallic surface in the COBRA-FTMW spectrometer with respect to the glass surfaces acting in the FM-mmW experiment. Within the former context, water is expected to play a crucial role: the hydrolytic pathway is supposed to proceed as long as water is available. In fact, the amount of water detected by means of low-frequency RER experiment as well as the residual water of the deuterated solvent is believed to be sufficient to observe the formation of the main species arising from HBA hydrolysis, i.e. BA at room temperature and PMI at higher temperatures.

On the other hand, the FM-mmW experiment can provide further clues 274 for a deeper understanding of the hydrolytic mechanism. At first, a tentative 275 generation of PMI in the gas phase has been carried out by thermolysis of HBA. 276 The solid was placed in a glass tube and heated up to 100 °C, also ensuring 277 a uniform heating along the path to the absorption cell. While heating the 278 sample up, a portion of the spectrum around 85.5 GHz was scanned in the 279 attempt of detecting two strong transitions of E-PMI, as predicted by our low-280 frequency measurements. No signal attributable to PMI (nor BN) was found. 281 Typically, the whole glass apparatus of the FM-mmW spectrometer is pumped 282 continuously, thereby removing water, although its residual presence cannot be 283 rule out. However, no metallic surfaces are available in the instrument, thus 284 leading to the formulation of two hypotheses for the lack of formation of PMI in 285 the FM-mmW experiment: (i) water is not available in a sufficient amount to 286 hydrolyze HBA; (ii) the metal catalysis is mandatory to obtain PMI from HBA 287 in gas phase. 288

To verify the reliability of spectral predictions and therefore rule out the pos-289 sibility of false negatives, we adopted a different production method, i.e. FVP. 290 By pyrolysis of two possible precursors of PMIⁱ, i.e. benzylamine and α -methyl 291 benzylamine, through dehydrogenation or elimination of CH_4 , respectively, a 292 small set of 27 transitions (belonging only to E-PMI) could be measured, with 293 the latter precursor leading to the highest S/N of the spectra. Conversely, the 294 use of N-methyl benzylamine gave no signals ascribable to the presence of PMI. 295 BN was found as a pyrolysis co-product, as proven by recording its rotational 296 transitions. While the PMI signal reached its maximum intensity by setting the 297 furnace temperature to 890 °C, the intensity of BN transitions kept increasing 298 up to 1200 °C. This confirms the prevalence of BN at higher temperatures, in 299 agreement with the low-frequency RER experiment. 300

Although a thorough analysis of the mechanisms taking place in the FVP 301 process is beyond the scope of this work, the FM-mmW experiment proved the 302 reliability of the centimeter-wave RER measurements and their extrapolation at 303 higher frequencies, but it left some unexplored areas concerning PMI formation 304 from HBA in the gas phase if no metallic surfaces are available. As mentioned 305 above, such possibilities could be further explored going beyond simple thermal 306 conditions. Several attempts to identify the Z isomer have been carried out, but 307 no signal ascribable to it was found. This might suggest that only the E isomer 308 is generated by flash vacuum pyrolysis, but we did not investigate further this 309 aspect in the present study. 310

ⁱFor a vacuum dynamic preparation of PMI, see ref. 49.

311 3 Conclusions

An easy and affordable approach based on hydrobenzamide thermolysis is pre-312 sented, which ensures to obtain phenylmethanimine both in gas-phase and in 313 solution as confirmed by rotational electric resonance (RER) and ¹H-nuclear 314 magnetic resonance (NMR) spectroscopy experiments, respectively. A detailed 315 structural and energetic description of phenylmethanimine has been carried out 316 by resorting to composite schemes for accurate results. This paved the way 317 for the registration and analysis of the microwave spectrum of both E- and Z-318 phenylmethanimine, leading to their first laboratory identification. This work 319 is a prerequisite for the possible radioastronomical detection of these species in 320 the interstellar medium, relying on accurate rotational rest frequencies. First, 321 in view of the strong chemical connection between benzonitrile and phenyl-322 methanimine, an astronomical search in the region Taurus Molecular Cloud 323 (TMC-1) is suggested. Finally, owing to the thorough analysis of RER and NMR 324 spectra at different temperatures, a possible mechanism of phenylmethanimine 325 formation by thermal tuning of hydrobenzamide, in which water is thought to 326 play a crucial role, is also proposed. 327

Associated Content

Supporting Information. Details on computational methodologies and spectroscopic RER and NMR techniques. Experimental details for the synthesis of
 HBA. Characterization of HBA. Copies of NMR spectra of HBA at different
 temperature. NMR check for BN absence in solution. List of all assigned RER
 transitions. Optimized structural parameters for the stationary points.

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Figure 5: Table of Contents Graphic

A multidisciplinary approach involving organic synthesis and high-resolution molecular spectroscopy has led to the definition of a thermally-tunable formation route for imines. Its application to phenylmethanimine combined with an integrated rotational spectroscopy - quantum chemistry protocol has enabled the full characterization of the latter, thus providing the means for future astronomical observations.