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An ab initio and DFT study of the valence isomers of pyridine

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Abstract

Ab initio (HF, MP2, and CCSD(T)) and density functional theory computed results on the equilibrium geometries, relative stabilities, strain energies, and vibrational spectra of the nine possible valence isomers of pyridine are reported. Although some aza-benzvalenes (**V1N** and **V3N**) lie lower in energy than Dewar pyridines (**D1N** and **D2N**), the strain energies for the latter are lower. Relative stabilities of the valence isomers, thermodynamic stability, and skeletal rigidity are comparable to those of benzene valence isomers. © 2001 Elsevier Science B.V. All rights reserved.

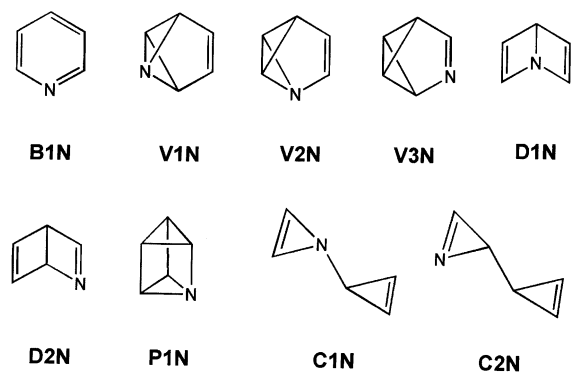
1. Introduction

Pyridine, the first group V heterobenzene has played a leading role in formulating the concept of aromaticity in heterocyclic chemistry, and opened up a host of other planar 6π heterocyclic systems, such as arsabenzene, germabenzene, silabenzene, etc. [1–5]. Replacing one of the methine groups in benzene by isoelectronic N seems to have negligible effect on the equilibrium structure, vibrational and electronic spectra [6–8]. While the planar monocyclic 6π systems led by benzene arguably occupied the central place, the study of their valence isomers also generated considerable interest. Inspired by the success in the synthesis of the valence isomers of benzene, quite a few computational studies of high sophistication appeared on this subject [9–12]. The X_6 isomers where all the CH groups are replaced by the trivalent X groups, such as $X = N, P, As$, and SiH , were subjects of various theoretical investigations [13–17]. It is in-

teresting to note that most of the valence isomers of phosphinine are synthetically accomplished [18,19], and a few theoretical studies on mono- and di-phosphinines appeared recently [20–22]. In contrast, chemistry of the valence isomers of pyridine is not much known. A recent matrix isolation study by Nakata et al. [23] reported the transient generation of the Dewar pyridine upon UV irradiation of pyridine and its IR characterization. However, the substituted isomers for the Dewar pyridine (e.g., Dewar picolines) and azaprismane are well known [24–29]. To our knowledge, experimental or theoretical calculations are missing about the aza-benzvalene and 3,3'-azabicyclopropenyl isomers, and their substituted analogues. While the effect of perturbation induced by the replacement of a CH group by the isoelectronic N group in the planar valence isomer of benzene has been a topic of many studies, studies on the effect of substitution on the other valence isomeric forms of benzene are scarce. Looking at the success in the synthesis of all the valence isomers of benzene and phosphinine, and the lack of it for the pyridine valence isomers

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Scheme 1. The nine valence isomers of pyridine, $(CH_5)N$, considered in this study.

(Scheme 1), prompted us to undertake a detailed computational study of all the valence isomers of pyridine and assess their synthetic viability from a thermodynamic point of view. Quantum mechanical calculations of the molecular structure and properties have become indispensable tools for understanding and predicting the bonding and reactivity features of medium-sized molecules. The present paper reports the first systematic computational results on the equilibrium structures, relative energies, strain energies and vibrational spectra of all the valence isomers of pyridine. Comparisons were made with their benzene and phosphinine counterparts and with the experimental results wherever possible. These studies provide a basis for the understanding of molecules, which are analogues of the valence isomers of benzene where more CH groups are replaced with heteroatoms [30].

2. Computational details

Geometry optimizations of all the valence isomers considered in this study were done using ab initio (HF and MP2) and hybrid density functional (B3LYP) methods. The present and previous calculations in related systems indicate that the 6-31G* basis set, in conjunction with electron correlated methods, adequately describes the geometry and energetics. All the structures considered in this study were characterized as minima on the potential energy surface by frequency calculations

performed at HF and B3LYP [31,32] levels using the 6-31G* basis set. Single point calculations were done at the CCSD(T)/6-31G* level on MP2/6-31G* geometries, after adjudging that MP2 provided better equilibrium geometries compared to B3LYP. Coupled cluster method with triples correction was expected to yield quantitatively reliable energetics in this class of compounds. MP2 single point calculations were done with the 6-311+G** basis set, which was of triple- ζ quality with added polarization and diffuse functions on main group elements and on hydrogens, respectively. The thermochemical data were obtained from the vibrational analysis performed at the B3LYP level, after scaling them with the factor of 0.98 [33,34]. Only the scaled frequencies are reported in the paper. All the calculations were done using the GAUSSIAN 94 suite of programs [35].

3. Results and discussion

The important skeletal parameters of the optimized geometries obtained at the MP2/6-31G* level are given in Fig. 1. Comparison with the previous experimental results for pyridine, and aza-prismane (here it is to be noted that the experimental geometry corresponds to a substituted aza-prismane) indicate that they are in good agreement with each other. In the aza-benzvalene isomers, the central C–C distance of the bicyclobutane moiety shows some interesting variations. Namely the C–N bond length in **V1N** is 1.475 Å, C–C is 1.426 Å in **V2N** and 1.455 Å in **V3N**. Thus in a similar position a C–N bond length is significantly longer than a C–C bond. Additionally, the C–C bond in **V2N** is substantially reduced compared to 1.453 Å obtained for the benzvalene moiety, a trend which was reproduced at HF, B3LYP, and MP2 levels. The unusually short C–C bond length in **V2N** was reflected in the high strain energy for this particular positional isomer (see later). Comparison of various bond lengths and bond angles at B3LYP/6-31G*, MP2/6-31G*, and MP2/6-31G** levels indicates no observable differences. But, HF/6-31G* consistently underestimates the bond lengths while the bond angles are in good agreement.

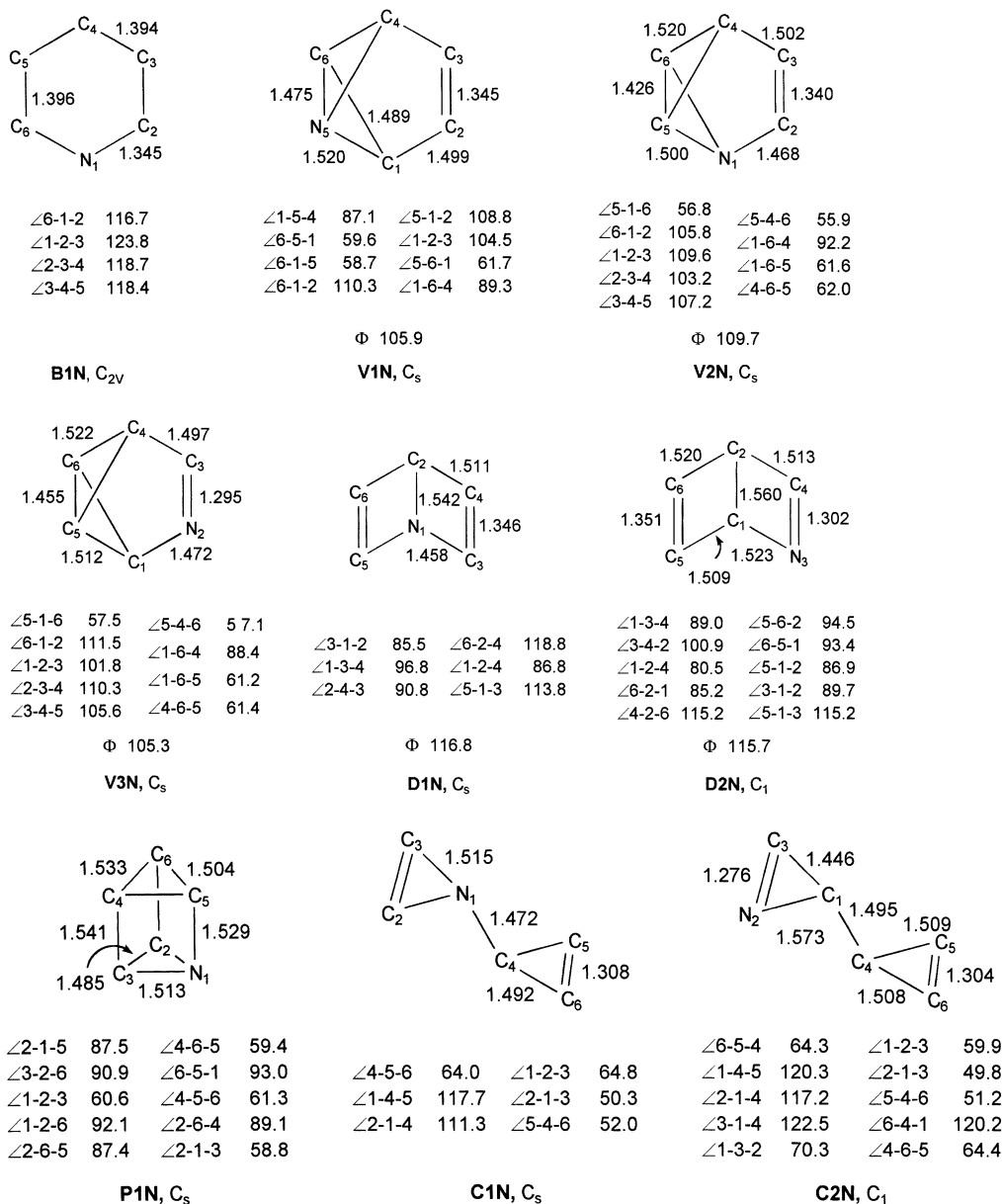


Fig. 1. Important geometric parameters of the valence isomers of pyridine obtained at MP2/6-31G* level. Bond lengths are in Å and angles are in degrees. Φ is the angle between the two planes formed by the three-membered rings in the bicyclobutane moiety in benzvalence and the four-membered rings in Dewar benzene isomers.

The total energies for all the valence isomers considered in the study at various levels of theory along with the zero point energy (ZPE) and enthalpy corrections (at 298 K) obtained at the B3LYP/6-31G* level of theory are given in Table 1.

Similar to our previous studies, we did the basis set correction at MP2 level and the best estimates for the relative energies were obtained following the equation below, which was shown to give excellent estimates for the relative energies [20,21].

Table 1

The total energies of the valence isomers of pyridine at various levels of theory^a

| Structure | HF/ 6-31G* | B3LYP/ 6-31G* | MP2/ 6-31G* | MP2/ 6-31G** | MP2/ 6-311+G** ^b | CCSD(T)/ 6-31G* ^b | ZPE ^c | Enthalpy correction ^{c,d} |
|------------|---------------|------------------|----------------|-----------------|--------------------------------|---------------------------------|------------------|---------------------------------------|
| B1N | −246.69582 | −248.28497 | −247.48253 | −247.52180 | −247.60892 | −247.55058 | 0.08904 | 0.09425 |
| V1N | −246.56650 | −248.16057 | −247.36984 | −247.40957 | −247.49905 | −247.43739 | 0.08667 | 0.09178 |
| V2N | −246.53986 | −248.13469 | −247.34185 | −247.38187 | −247.47077 | −247.41034 | 0.08550 | 0.09067 |
| V3N | −246.57929 | −248.17061 | −247.37963 | −247.41967 | −247.50818 | −247.44639 | 0.08682 | 0.09185 |
| D1N | −246.54484 | −248.14369 | −247.34656 | −247.38640 | −247.47688 | −247.41773 | 0.08603 | 0.09140 |
| D2N | −246.56651 | −248.15886 | −246.36291 | −247.40254 | −247.49239 | −247.43567 | 0.08626 | 0.09161 |
| P1N | −246.48965 | −248.08689 | −247.29051 | −247.33096 | −247.42080 | −247.35963 | 0.08618 | 0.09104 |
| C1N | −246.44545 | −248.04440 | −247.24591 | −247.28543 | −247.37819 | −247.31845 | 0.08015 | 0.08715 |
| C2N | −246.51443 | −248.10757 | −247.31194 | −247.35155 | −247.44105 | −247.38277 | 0.08253 | 0.08927 |

^a Zero point and enthalpy corrections are given at B3LYP/6-31G* level only. All values are given in Hartrees.^b Single point calculations on MP2/6-31G* geometries.^c ZPE and enthalpy corrections are obtained at B3LYP/6-31G* level.^d Enthalpy correction is obtained at 298 K.

$$\Delta E = \Delta E_{\text{CCSD(T)}} + \Delta E_{(\text{MP2/6-311+G}^{**}-\text{MP2/6-31G}^*)} + \Delta H, \quad (1)$$

where ΔH is the enthalpy correction factor obtained by the B3LYP/6-31G* method. The discussion of energetics from now on will be based on the best estimated unless otherwise specified. Strain energies for these valence isomers were obtained using our previous strategy for the phosphinine isomers [21], which was put forward by Hiberty et al. [22]. In view of the fact that benzene and pyridine have very similar resonance energies,

a value of 25 kcal mol^{−1} was taken as the resonance energy of pyridine [12].

$$S(\mathbf{X}) = E(\mathbf{X}) - E(\mathbf{B1N}) + \sum \text{BS}_i(\mathbf{X}) - 678. \quad (2)$$

Here $S(\mathbf{X})$ is defined as the strain energy, $E(\mathbf{X}) - E(\mathbf{B1N})$ as the relative energy of isomer \mathbf{X} with respect to **B1N** and $\sum \text{BS}_i(\mathbf{X})$ is obtained by summing the standard bond strengths. However, in this approach identical bond strengths are assumed for a given type of bond in different molecules and to that end the calculated strain energies are only approximate estimates.

Table 2

The relative energies for all the valence isomers of pyridine obtained at various levels of theory^a

| Structure | HF/ 6-31G* | B3LYP/ 6-31G* | MP2/ 6-31G* | MP2/ 6-31G** | MP2/ 6-311+G** ^b | CCSD(T)/ 6-31G* ^b | Best estimate ^c | Sum of bond strengths ^d | Strain energy |
|------------|---------------|------------------|----------------|-----------------|--------------------------------|---------------------------------|-------------------------------|---------------------------------------|------------------|
| B1N | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 653 | — ^e |
| V1N | 81.1 | 78.1 | 70.7 | 70.4 | 68.9 | 71.0 | 67.7 | 675 | 64.7 |
| V2N | 97.9 | 94.3 | 88.3 | 87.8 | 86.7 | 88.0 | 84.2 | 675 | 81.2 |
| V3N | 73.1 | 71.8 | 64.6 | 64.1 | 63.2 | 65.4 | 62.5 | 683 | 67.5 |
| D1N | 94.7 | 88.7 | 85.3 | 85.0 | 82.9 | 83.4 | 79.1 | 660 | 61.1 |
| D2N | 81.1 | 79.1 | 75.1 | 74.8 | 73.1 | 72.1 | 68.5 | 668 | 58.5 |
| P1N | 129.4 | 124.3 | 120.5 | 119.8 | 118.1 | 119.8 | 115.4 | 690 | 127.4 |
| C1N | 157.1 | 151.0 | 148.5 | 148.3 | 144.8 | 145.7 | 137.5 | 660 | 119.5 |
| C2N | 113.8 | 111.3 | 107.0 | 106.8 | 105.3 | 105.3 | 100.5 | 668 | 90.5 |

^a The best estimates from Eq. (1), cumulative bond strengths and strain energies calculated by Eq. (2) are also given. All the values are given in kcal mol^{−1}.^b Single point calculations on MP2/6-31G* geometries.^c Best estimate is obtained from Eq. (1) for all the structures.^d The bond strengths of C–C, C=C, C–N and C=N are 80, 145, 70, and 133 kcal mol^{−1}, respectively. Taken from (a) W. Kutzelnigg, Angew. Chem. Int. Ed. Engl. 23 (1984) 272 and (b) M.W. Schmidt, P.N. Truong, M.S. Gordon, J. Am. Chem. Soc. 109 (1987) 5217.^e Pyridine, **B1N** is taken as the reference.

A quick look at the relative energies reveals interesting subtle variations when compared to benzene and phosphinine valence isomers which point to the involvement of intricate factors in governing the relative stabilities. One striking feature is that, given a choice, nitrogen always prefers to occupy an sp^2 centre compared to sp^3 centre without exception. Thus, in aza-benzvalene, dewar benzvalene and aza-3, 3'-bicyclopentenyl isomers, **V3N**, **D2N** and **C2N** positional isomers, where N occupies an sp^2 centre, were found to be the most stable positional isomers, in their respective categories.

It is to be noted that the chemistry of aza-benzvalene isomers or their substituted derivatives is virtually unexplored, whereas quite a few derivatives of Dewar pyridines and aza-prismane

were synthesized long ago. The relative energetics show that two of the aza-benzvalenes (**V1N** and **V3N**) are lower in energy compared to the Dewar pyridines. However, all the three aza-benzvalene isomers were calculated to be more strained than both the Dewar pyridine isomers. We may recall that the chronology of the synthesis of benzene isomers closely resembles their strain energies, i.e., the isomers with lower strain energies have become synthetically available earlier. Therefore, it is not surprising to see that Dewar pyridines were synthesized prior to the synthesis of aza-benzvalenes. However, considering the comparable strain energies for the aza-benzvalene isomers and Dewar pyridine isomers, the present study predicts that the synthesis of aza-benzvalenes should be soon coming up.

Table 3

The harmonic frequencies (cm^{-1}) of the valence isomers of pyridine obtained at the B3LYP/6-31G* level

| Structure | Harmonic frequencies (in cm^{-1}) |
|-------------------------|---|
| B1N (C_{2v}) | 378.1 (A2), 413.6 (B1), 601.7 (A1), 656.8 (B2), 704.2 (B1), 747.8 (B1), 879.7 (A2), 937.6 (B1), 973.7 (A2), 989.7 (B1), 991.6 (A1), 1030.3 (A1), 1065.2 (B2), 1078.5 (A1), 1157.8 (B2), 1228.1 (A1), 1282.2 (B2), 1370.1 (B2), 1458.1 (B2), 1500.3 (A1), 1605.3 (B2), 1611.8 (A1), 3107.2 (B2), 3109.3 (A1), 3128.3 (A1), 3143.4 (B2), 3151.5 (A1) |
| V1N (C_s) | 505.2 (A'), 523.2 (A''), 610.0 (A'), 704.8 (A'), 739.0 (A''), 750.1 (A'), 822.3 (A''), 855.7 (A'), 872.4 (A''), 880.1 (A''), 972.7 (A'), 978.6 (A''), 983.7, (A'), 1053.2 (A''), 1092.3 (A'), 1120.5 (A'), 1196.0 (A'), 1218.2 (A''), 1271.1 (A''), 1332.8 (A''), 1376.4 (A'), 1615.2 (A'), 3111.6 (A'), 3153.2 (A''), 3156.2 (A'), 3183.6 (A''), 3206.6 (A') |
| V2N (C_s) | 514.6 (A''), 519.4 (A''), 635.2 (A''), 717.8 (A'), 728.7 (A''), 753.9 (A''), 773.2 (A'), 822.0 (A'), 847.1 (A'), 853.4 (A''), 877.4 (A'), 958.2 (A''), 958.8 (A'), 1006.6 (A'), 1061.8 (A''), 1084.9 (A''), 1104.4 (A'), 1159.7 (A'), 1225.6 (A'), 1298.3 (A'), 1403.0 (A'), 1613.9 (A'), 3124.0 (A'), 3157.4 (A''), 3176.8 (A'), 3189.4 (A'), 3215.1 (A') |
| V3N (C_s) | 511.1 (A''), 564.4 (A''), 695.7 (A'), 718.6 (A''), 760.0 (A'), 792.7 (A''), 821.2 (A') 859.1 (A'), 882.5 (A'), 883.3 (A''), 905.9 (A''), 966.2 (A'), 990.1 (A''), 1029.2 (A'), 1101.0 (A''), 1112.8 (A''), 1180.9 (A'), 1198.5 (A'), 1249.7 (A'), 1303.6 (A'), 1392.5 (A'), 1620.6 (A'), 3140.8 (A'), 3156.3 (A'), 3163.2 (A''), 3166.9 (A'), 3182.2 (A') |
| D1N (C_s) | 378.3 (A''), 394.0 (A'), 502.5 (A'), 714.5 (A''), 774.0 (A'), 800.5 (A''), 821.4 (A'), 862.0 (A''), 871.0 (A'), 915.1 (A'), 929.0 (A'), 963.4 (A'), 977.5 (A''), 1028.6 (A''), 1105.1 (A''), 1108.5 (A'), 1154.4 (A'), 1199.8 (A''), 1266.2 (A''), 1271.2 (A'), 1578.0 (A''), 1608.8 (A'), 3055.6 (A'), 3162.2 (A''), 3164.4 (A'), 3199.7 (A''), 3201.9 (A') |
| D2N (C_1) | 341.6 (A), 395.8 (A), 485.6 (A), 734.9 (A), 799.4 (A), 823.8 (A), 862.4 (A), 874.3 (A), 896.7 (A), 943.6 (A), 944.8 (A), 959.7 (A), 979.0 (A), 1056.5 (A), 1145.4 (A), 1156.2(A), 1190.0 (A), 1193.8 (A), 1270.8 (A), 1290.4 (A), 1587.8 (A), 1621.6 (A), 3061.7 (A), 3082.9 (A), 3095.1 (A), 3140.0 (A), 3170.7 (A) |
| P1N (C_s) | 633.3 (A''), 699.0 (A'), 743.2 (A''), 748.3 (A'), 790.3 (A''), 800.0 (A'), 842.8 (A''), 863.5 (A''), 872.0 (A'), 944.4 (A'), 953.3 (A'), 968.8 (A''), 986.6 (A''), 1003.1 (A'), 1013.2 (A''), 1053.9 (A'), 1135.1 (A'), 1163.0 (A''), 1219.0 (A'), 1262.6 (A''), 1305.2 (A'), 1333.4 (A'), 3124.2 (A''), 3136.4 (A'), 3138.6 (A'), 3163.0 (A''), 3174.0 (A') |
| C1N (C_s) | 64.0 (A''), 243.7 (A''), 312.3 (A'), 432.3 (A'), 443.2 (A''), 558.4 (A'), 590.9 (A'') 618.2 (A'), 711.0 (A''), 834.0 (A''), 850.0 (A''), 875.1 (A'), 931.8 (A'), 940.8 (A'') 971.9 (A'), 1030.9 (A''), 1062.6 (A''), 1092.7 (A'), 1199.3 (A'), 1356.2 (A'), 1698.4 (A'), 1763.1 (A'), 2941.8 (A'), 3197.2 (A''), 3230.2 (A''), 3240.1 (A'), 3288.9 (A') |
| C2N (C_1) | 71.0 (A), 230.9 (A), 284.1 (A), 413.8(A), 500.6 (A), 602.4 (A), 693.7 (A), 770.2 (A), 794.8 (A), 842.4 (A), 917.1 (A), 990.9 (A), 1014.7 (A), 1026.2 (A), 1053.0 (A), 1060.1 (A), 1179.5 (A), 1276.3 (A), 1307.7 (A), 1420.2 (A), 1701.8 (A), 1720.7 (A), 2999.6 (A), 3052.6 (A), 3136.0 (A), 3198.6 (A), 3242.1 (A) |

All the vibrational modes, for each of the isomers considered in the study, are depicted in Tables 2 and 3 along with their symmetry labels. Comparison of the present B3LYP/6-31G* spectra with the experimental vibrational spectra for pyridine and Dewar pyridine indicates reasonable agreement between computation and experiment [25]. Nonetheless, comparison of the present results with previous calculations and the experimental spectra of pyridine and Dewar pyridine indicate that using the 6-31++G** basis set improves the results further. Table 3 indicates that all the polyhedral isomers of pyridine have a strong skeletal framework similar to their benzene analogues, as reflected in their definitive large magnitudes for all the normal modes, similar to those of benzene valence isomers indicating a stronger skeletal framework.

4. Conclusions

Ab initio and DFT calculations confirm that all the valence isomers are minima on their respective potential energy surfaces. Comparison of the relative energies of the pyridine valence isomers with those of benzene and phosphinine indicates that the energy difference between the planar isomers and the non-planar ones is the highest for pyridine. The computed results indicate that two of the aza-benzvalenes are lower in energy compared to both the Dewar pyridines. The apparent ease of experimental accomplishment of Dewar pyridines compared to aza-benzvalenes may be traced to their strain energies. Comparison of the magnitude of the harmonic frequencies with the benzene analogues indicates close resemblance to each other.

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