

# A computational study of the valence isomers of benzene and their group V hetero analogs

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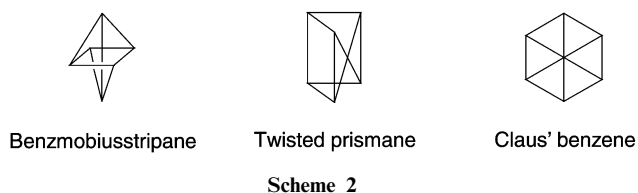
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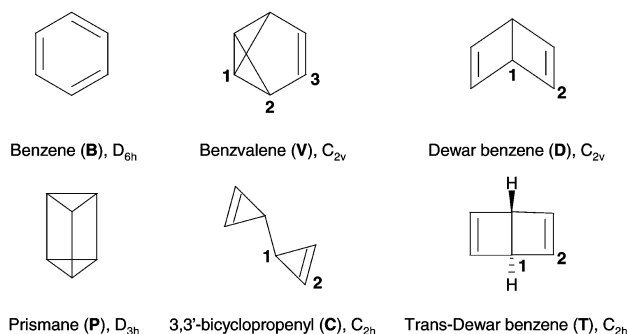
*Ab initio* [HF, MP2 and up to CCSD(T)] and hybrid density functional B3LYP calculations were performed on benzene, group V heterobenzenes,  $(\text{CH})_5\text{X}$  ( $\text{X} = \text{N}, \text{P}$  and  $\text{As}$ ), and their corresponding valence isomers. Six valence isomers of benzene and ten valence isomers of  $(\text{CH})_5\text{X}$  have been identified and their structures, energetics, relative stabilities and their reactivities were studied. The stability ordering observed in phosphinine and arsabenzene isomers is very similar to that in the benzene isomers (benzene > benzvalene > Dewar benzene > prismane > bicyclopropenyl > *trans*-Dewar benzene). In the pyridine isomers, one of the bicyclopropenyl isomers (**C2N**) is computed to be more stable than the prismane isomer (**P1N**). The framework is the main factor determining the relative stabilities and the nature of the substituent is of secondary importance. Exactly the same trend in the relative energies is observed for phosphinine and arsabenzene isomers.

The close resemblance between benzene and pyridine in terms of spectra, structure and other properties demonstrates that replacement of one methine group of benzene by an isoelectronic group does not disrupt aromaticity and is chiefly responsible for the formulation of the concept of aromaticity.<sup>1–3</sup> Phosphinine and arsabenzene, resulting from the replacement of the methine group by P and As, respectively, were demonstrated to also be aromatic compounds.<sup>4–9</sup> The five well-known classical valence isomers of benzene (**B**), benzvalene (**V**), Dewar benzene (**D**), prismane (**P**), bicyclopropenyl (**C**) and the recently conceived *trans*-Dewar benzene (**T**) constitute the plausible  $(\text{CH})_6$  valence isomers (Scheme 1).<sup>10–12</sup> In addition to these isomers, Balaban's benzmöbiusstrip, the twisted prismane proposed by Karl and Bauer, and Claus' benzene, all of which have identical connectivities are other possibilities (Scheme 2).<sup>13,14</sup> However, these are chemically unrealistic. The syntheses of all the classical isomers except for *trans*-Dewar benzene (**T**) have been achieved, and these form the subjects of a number of theoretical and experimental investigations.<sup>10–12</sup> While the hetero analogs of the planar benzene are one of the most extensively studied topics by experimentalists and theoreticians alike, the study of the other valence isomers has also attracted considerable attention, especially from the experimentalists.<sup>15,16</sup> Most of the valence isomers of phosphinine were synthesized and were found to undergo interesting rearrangement reactions and to possess

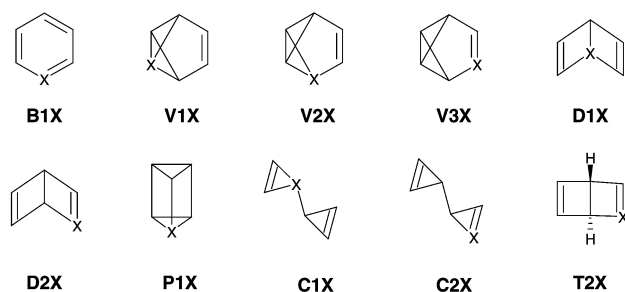


novel binding capabilities as ligands to transition metal templates.<sup>15</sup> Transient generation of the Dewar pyridine (**D1N**) through UV irradiation of pyridine was reported recently.<sup>16b</sup> It is to be noted that the substituted Dewar pyridines and azaprismanes are well-known.<sup>16</sup> However, the data on azabenzvalenes (**V1N**, **V2N** or **V3N**) and 3,3'-azabicyclopropenyl isomers or their substituted isomers are scarce. Although arsabenzene has been known for quite some time the chemistry of its other valence isomeric forms is relatively unknown. Replacement of one or more of the methine groups in the benzenoid framework by isovalent groups has become one of the most hotly pursued topics in contemporary heterocyclic chemistry, both by theoreticians and experimentalists.<sup>6–8,17–22</sup> The chemistry of the valence isomers of  $\text{X}_6$  ( $\text{X} = \text{N}, \text{P}, \text{As}$ , and  $\text{SiH}$ ), where all the methine groups are replaced by isovalent groups, was extensively studied by computational means.<sup>21,22</sup> However, little theoretical attention has been paid to the valence isomers of group V analogs of benzene until recently, and our preliminary reports on the valence isomers of pyridine and phosphinine form the first quantitative computational studies in this direction.<sup>23</sup> Computational studies are invaluable tools in obtaining insights into this class of compounds. Examination of the equilibrium geometries, characterization of the minima on the potential energy surface, and the relative energies of the valence isomers of group V heterobenzenes and their comparison with the parent benzene counterparts provide a basis to assess the variation induced by the heteroatom.

The present study is aimed at providing accurate equilibrium geometries and relative stabilities of the valence isomers of pyridine (**B1N**), phosphinine (**B1P**) and arsabenzene (**B1As**). Benchmark calculations were done on benzene to test the suitability of popular theoretical models by comparing with the



Scheme 1



Scheme 3

available experimental data and other high level theoretical calculations. The ten plausible classical valence isomers of  $(\text{CH})_5\text{X}$  ( $\text{X} = \text{N}, \text{P}$  and  $\text{As}$ ), where one of the methine groups is replaced by the isovalent atom, one benzene (**B1X**), three benzvalenes (**V1X**, **V2X**, and **V3X**), two Dewar benzenes (**D1X** and **D2X**), one prismane (**P1X**), two bicyclopropenyls (**C1X** and **C2X**) and one *trans*-Dewar benzene (**T2X**), were subjected to detailed post-SCF *ab initio* and DFT calculations (Scheme 3).

## Methodology

All the calculations were done using the Gaussian 94 suite of programs.<sup>24</sup> The geometries of all the structures were fully optimized within the symmetry constraints, initially at the HF/6-31G\* level. Further refinement of geometries was done at the B3LYP<sup>25</sup> and MP2 levels using the 6-31G\* basis set. The effect on the geometry of these compounds of adding a set of polarization functions to the peripheral hydrogens was tested by doing an optimization using the 6-31G\*\* basis set at the MP2 level. The MP2/6-31G\* and MP2/6-31G\*\* geometries are virtually identical, indicating that 6-31G\* is adequate in giving proper equilibrium geometries. The nature of the stationary points obtained was characterized by frequency calculations at the HF and B3LYP levels, which designate all the valence isomers considered in the study as local minima. The present and previous studies indicate that MP2 gives better equilibrium geometries;<sup>19a</sup> single point calculations were done at the CCSD(T)/6-31G\* and MP2/6-311+G\*\* levels. The MP2 single point calculation with the 6-311+G\*\* basis set accounts for the basis set effects. A recent study on the diphosphinines and their valence isomers indicates that a single determinantal approach is adequate to get reliable results for this class of compounds.<sup>19a</sup> The enthalpy correction to the total energy is obtained by using the vibrational frequency data at the B3LYP level. The best estimates for the relative energies were obtained for all the molecules considered in this study, using eqn. (1):

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

$\Delta H$  is the enthalpy correction factor obtained by frequency calculations at the B3LYP/6-31G\* level. Although the CCSD(T) method is a reliable theory, the basis set of 6-31G\* quality is not adequate. Performing uniform calculations with triple- $\zeta$  quality basis sets for all the species considered in this study is beyond our available computational facilities. Therefore, our scheme of best estimates, which accounts for the CCSD(T) basis set deficiency, at the MP2 level, is designed to circumvent this problem. This scheme seems to be in excellent agreement with the high level calculations on benzene isomers and the available experimental results.

## Results and discussion

The discussion on the valence isomers of the model system is done as a reference as well as to test the suitability of the

adopted computational tools in modeling the systems under study. The equilibrium geometries of all the valence isomers are compared and contrasted among themselves as well as with the reference pristine isomers. Similarly, the relative energies of the valence isomers of benzene are taken as a reference to assess the relative energy ordering of its group V counterparts.

### Equilibrium geometries

Fig. 1 depicts the MP2/6-31G\* optimized geometries and their comparison with the experimental data, where available, for benzene isomers. The MP2 geometries are in excellent agreement (maximum deviation of 0.012 Å in bond length) with the QCISD/6-311G\* geometries.<sup>10b</sup> The computed geometries are in reasonable agreement with the available experimental numbers, and will form our reference values to estimate the perturbation in the skeletal bond lengths upon replacing the methine groups with the isovalent atoms. A recent computational study that considered the five classical valence isomers, confirms the suitability of the MP2 level in obtaining reliable geometries.<sup>10b</sup> The less explored *trans*-Dewar benzene (**T**) isomer has a substantially shorter central single bond and fairly longer double bond lengths.

The principal geometric parameters of the substituted benzenes (**B1X**), benzvalenes (**V1X**, **V2X** and **V3X**), Dewar benzenes (**D1X** and **D2X**), prismanes (**P1X**), bicyclopropenyls (**C1X** and **C2X**) and *trans*-Dewar benzenes (**T2X**) obtained at the HF, B3LYP and MP2 levels of theory with the 6-31G\* basis set are given in Fig. 2–7 respectively. The numbering for the individual positional isomers has to be deciphered from Scheme 1.

Pyridine (**B1N**), phosphinine (**B1P**) and arsabenzene (**B1As**) are found to have bond lengths corresponding to aromatic compounds (Fig. 2), a result which is consistent with previous studies.<sup>5,18</sup> In all the isomers, B3LYP and MP2 geometries are in good agreement, with HF consistently underestimating the bond lengths. The C–C bond lengths in the three compounds are similar to the C–C bond length in benzene, with a maximum deviation of only 0.005 Å in **B1As**. In addition to this, the C–X bond lengths in these compounds are in-between the normal C–X single and double bond lengths, supporting full delocalization. In general, among the benzvalene isomers, the substitution pattern or the type of substitution does not seem to perturb the skeleton significantly in a majority of the cases. Among the benzvalene valence isomers (Fig. 3) all the C–C bonds in the positional isomers are very similar and are closer to those of the corresponding pristine molecules. Obviously, the C–X bonds are different due to the different atomic radii of

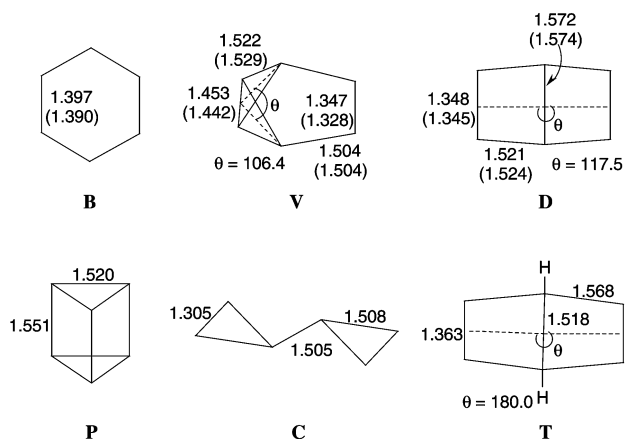
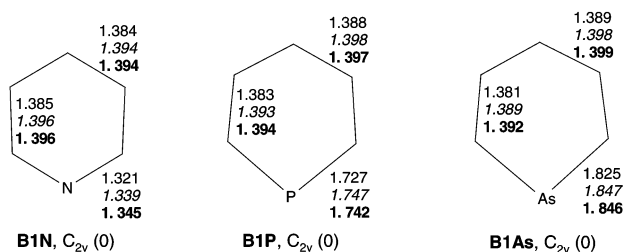


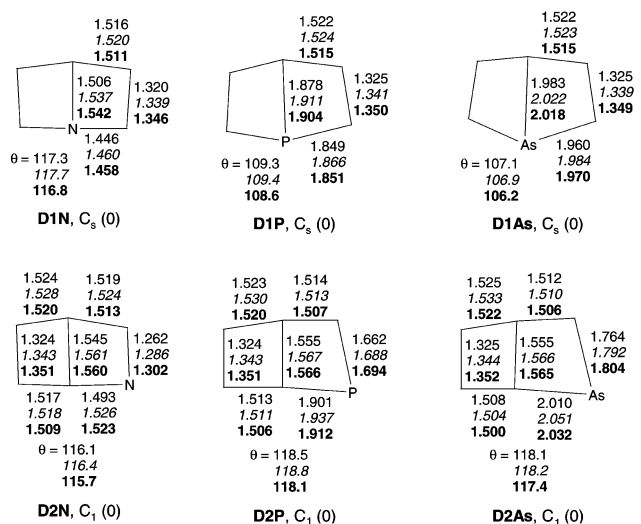
Fig. 1 The principal geometric parameters of the valence isomers of benzene obtained at the MP2/6-31G\* level. Experimental parameters are given in parentheses wherever available. The bond lengths are in Å and the angles are in degrees.



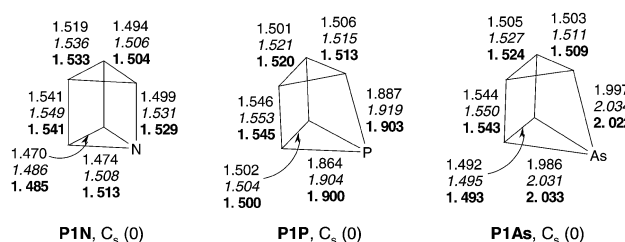
**Fig. 2** The principal geometric parameters of pyridine (**B1N**), phosphinine (**B1P**) and arsabenzene (**B1As**) obtained at the HF (plain), B3LYP (italics) and MP2 (bold) levels using the 6-31G\* basis set. All values are given in Å.

the substituted atom X. The bridge-head C–C bond of the bicyclobutane moiety in **V2N** is substantially shorter compared to the parent molecule, while every other isomer, **V2P**, **V2As**, **V3N**, **V3P** and **V3As**, have bond lengths similar to the unsubstituted benzvalene.

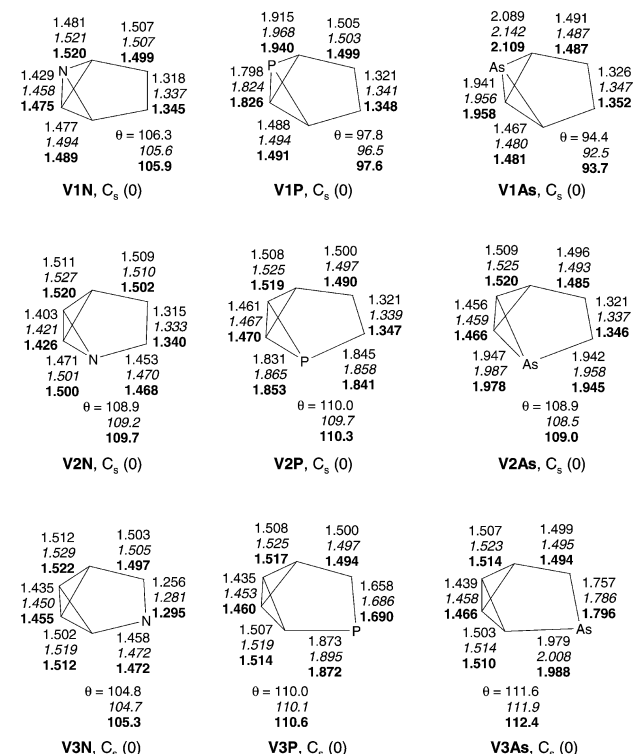
A close look at the Dewar benzene positional isomers (Fig. 4) indicates that the heteroatom substitution does not make any significant perturbation to the skeleton in terms of bond lengths. In general, the computed C–C single and double bond lengths are essentially identical to those in the parent molecule, irrespective of the substituent size and site. The angle between the two planes ( $\theta$ ) is similar, except in **D1P** and **D1As** when P and As are substituted at the bridge head position, resulting in a reduction of  $\theta$  by approximately 10°. The prismane valence isomers (Fig. 5) also do not show any significant deviations in the bond lengths compared to the parent molecules. In **C2N** (Fig. 6), the C–N single bond length is found to be longer than a normal C–N bond. Even in the same compound, the C–C single bond (1.446 Å) is computed to be much shorter than the C–N single bond. Interestingly, the bond lengths in **C1X** and



**Fig. 4** The principal geometric parameters of the Dewar benzene isomers (**D1X** and **D2X**) obtained at the HF (plain), B3LYP (italics) and MP2 (bold) levels using the 6-31G\* basis set. The bond lengths are in Å and the angles are in degrees.



**Fig. 5** The principal geometric parameters of the prismane isomers (**P1X**) obtained at the HF (plain), B3LYP (italics) and MP2 (bold) levels using the 6-31G\* basis set. All values are given in Å.

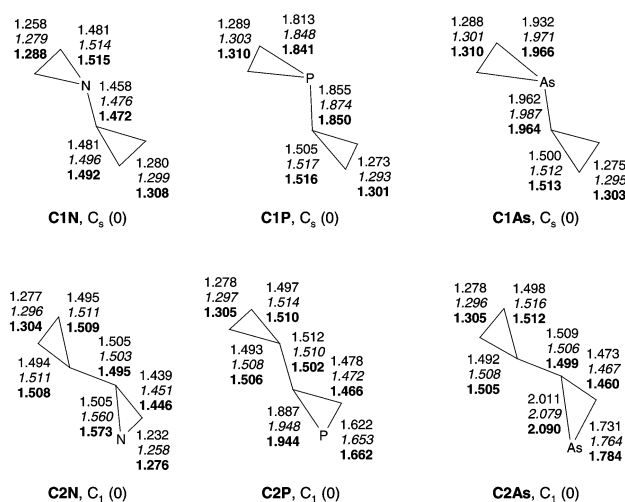


**Fig. 3** The principal geometric parameters of the benzvalene isomers (**V1X**, **V2X** and **V3X**) obtained at the HF (plain), B3LYP (italics) and MP2 (bold) levels using the 6-31G\* basis set. The bond lengths are in Å and the angles are in degrees.

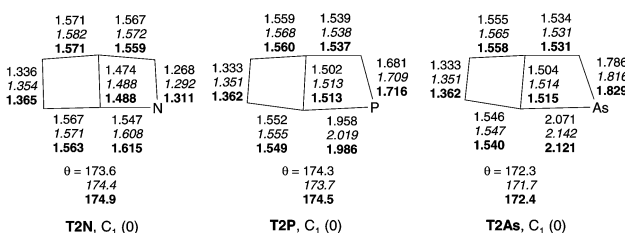
**C2X** (X = P and As) are found to be comparable to the corresponding standard bond lengths.

In all **T2X** (Fig. 7), the bridging bond is substantially shrunk compared to the bridging bond in the corresponding *cis* isomer (**D2X**), with **T2N** exhibiting the maximum effect. Similar to the situation in the parent isomers, most other bond lengths exhibit exactly the opposite trend, that is, elongation when compared to the corresponding **D2X** isomers. The C–N single bond length in **T2N** is substantially elongated, and **T2P** and **T2As** also show similar trends, albeit to a smaller extent. This feature is indicative of strain in the system and indicates the possibility of ring opening through C–X cleavage.

Therefore, the present analysis indicates that the replacement of a methine group by N, P, or As in the skeletons of the valence isomers of benzene does not induce noticeable skeletal perturbations. While the Hartree–Fock method consistently underestimates bond lengths for well known reasons, B3LYP and MP2 are in fairly good agreement with each other in most of the cases. In general, the B3LYP method overestimates bond lengths, especially for P and As valence isomers, with maximum deviation of 0.033 Å in the bond lengths and 1.5° in the bond angles. The change of basis set at the MP2 level to 6-31G\*\* did not result in any noticeable changes in geometric parameters, with almost identical results to the first three decimal places in bond lengths (maximum deviation 0.005 Å) and to the first decimal for bond angles (maximum deviation 0.2°). The discussion on the structures will be based on the MP2/6-31G\* geometries throughout the rest of the study unless otherwise stated.



**Fig. 6** The principal geometric parameters of the bicyclopropenyl isomers (**C1X** and **C2X**) obtained at the HF (plain), B3LYP (italics) and MP2 (bold) levels using the 6-31G\* basis set. All values are given in Å.



**Fig. 7** The principal geometric parameters of the *trans*-Dewar benzene isomers (**T2X**) obtained at the HF (plain), B3LYP (italics) and MP2 (bold) levels using the 6-31G\* basis set. The bond lengths are in Å and the angles are in degrees.

## Energetics

In this section, taking the valence isomers of benzene as a test case, for which experimental or highly reliable theoretical data is available, the performance of various levels of theory in giving reliable energetics for this class of compounds is assessed. A comparison will enable us to determine the strengths and drawbacks of various levels of theory and help us in choosing the most appropriate method to apply to the valence isomers of the compounds under study. The relative energies for all the valence isomers of benzene obtained at

different levels of theory are given in Table 1. Previously reported relative energies from G2 methods and experimental heats of formation wherever available are also given in the same table.<sup>10</sup> Expectedly, the HF method was not good for quantitative results and the dynamic electron correlation is essential in obtaining reliable energetics. Surprisingly, the B3LYP/6-31G\* method also considerably overestimates the stability of benzene, which results in the consistent underestimation of all other isomers. This problem may be traced to the limitations of the B3LYP, as well as most DFT based methods, in comparing the energies between  $\pi$ -delocalized and localized structures along the potential energy surface.<sup>26</sup> Virtually identical values are obtained at the MP2/6-31G\* and MP2/6-31G\*\* levels for all the isomers. These results point to the limitations of the CCSD(T) calculations when used in combination with an inadequate basis set such as 6-31G\*. However, the basis set correction done at the MP2 level [eqn. (1)] seems to have remedied the situation. Thus, excellent agreement is observed between our best estimates (this work) and the reported higher level calculations. Therefore, the relative energies obtained for the valence isomers of pyridine (**B1N**), phosphinine (**B1P**) and arsabenzene (**B1As**) by this procedure are likely to be very similar at further higher levels of theory.

The relative energies obtained at various levels of theory for all the valence isomers of pyridine (**B1N**), phosphinine (**B1P**) and arsabenzene (**B1As**) considered at various levels of theory is given in Tables 2, 3 and 4, respectively. Both the HF and the B3LYP levels consistently overestimate the stability of the delocalized conjugated systems. Adding a set of polarization functions on peripheral hydrogens, by going to a 6-311+G\*\* quality basis set, marginally improves the energetics, especially for the 3,3'-bicyclopropenyl and *trans*-Dewar benzene isomers. In contrast, MP2 gives a consistently better agreement and increased basis set quality over the 6-31G\* one gives only a minor improvement in the relative energies. Therefore, dynamic electron correlation is essential in obtaining accurate energetics, and double- $\zeta$  basis sets augmented with a set of polarization functions are expected to yield reliable energies. However, in this class of compounds the conventional *ab initio* methods perform much better than the currently popular density functional theory based methods.

The discussion on energetics will be based on the best estimates unless otherwise specified. The plot of the best estimates of all the valence isomers of benzene, pyridine, phosphinine and arsabenzene is given in Fig. 8. As reported earlier, the five valence isomers of benzene span a wide range of stabilities (up to 150.4 kcal mol<sup>-1</sup>) with *trans*-Dewar benzene (**T**) being the least stable (Table 1). This

**Table 1** The relative energies (kcal mol<sup>-1</sup>) of the valence isomers of benzene obtained at various levels of theory. Best estimates obtained using eqn. (1) are also given. Experimental values and high level theoretical estimates from the literature are given for comparison. The total energies (in parentheses) are in hartrees. The heats of formation for benzene, both experimental and calculated at various CBS and G2 levels, are given in kcal mol<sup>-1</sup> (in parentheses)

Struct.	HF/ 6-31G*	B3LYP/ 6-31G*	MP2/ 6-31G*	MP2/ 6-31G**	MP2/ 6-311+G** <sup>a</sup>	CCSD(T)/ 6-31G* <sup>a</sup>	Best estimate	G2 (MP2,G2 SVP) <sup>b</sup>	G2 (MP2) <sup>b</sup>	G2 (MP3) <sup>b</sup>	G2 G2 <sup>b</sup>	CBS- Q <sup>b</sup>	CBS- APNO <sup>b</sup>	Expt. <sup>c</sup>
<b>B</b>	0.0 (-230.70314)	0.0 (-232.24866)	0.0 (-231.45773)	0.0 (-231.50539)	0.0 (-231.58383)	0.0 (-231.53074)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
<b>V</b>	83.0	81.2	74.5	74.0	73.0	75.0	71.7	71.6	71.3	71.7	71.4	73.3	73.8	67.1
<b>D</b>	86.5	84.4	80.4	80.2	79.0	77.7	74.6	76.0	75.6	75.5	75.5	78.5	78.6	67.3
<b>P</b>	125.4	121.5	117.7	117.0	116.2	117.7	114.1	112.5	112.0	112.5	112.2	113.7	114.6	—
<b>C</b>	130.8	127.9	125.5	125.4	123.9	125.1	119.9	118.6	118.1	117.8	118.0	121.4	121.6	—
<b>T</b>	178.0	163.9	162.3	161.4	158.7	156.5	150.4	—	—	—	—	—	—	—

<sup>a</sup> Single point calculations on MP2/6-31G\* optimized geometries. <sup>b</sup> Values are taken from ref. 10a. <sup>c</sup> Experimental values from S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *J. Phys. Chem. Ref. Data*, Suppl. No. 1, 1998.

**Table 2** The relative energies (kcal mol<sup>-1</sup>) of the valence isomers of pyridine obtained at various levels of theory. Best estimates obtained using eqn. (1) are also given. Total energies, given in parenthesis, are in hartrees

Structure	HF/6-31G*	B3LYP/6-31G*	MP2/6-31G*	MP2/6-31G**	MP2/6-311+G** <sup>a</sup>	CCSD(T)/6-31G* <sup>a</sup>	Best estimate
<b>B1N</b>	0.0 (-246.69582)	0.0 (-248.28497)	0.0 (-247.48253)	0.0 (-247.52180)	0.0 (-247.60892)	0.0 (-247.55058)	0.0
<b>V1N</b>	81.1	78.1	70.7	70.4	68.9	71.0	67.7
<b>V2N</b>	97.9	94.3	88.3	87.8	86.7	88.0	84.2
<b>V3N</b>	73.1	71.8	64.6	64.1	63.2	65.4	62.5
<b>D1N</b>	94.7	88.7	85.3	85.0	82.9	83.4	79.1
<b>D2N</b>	81.1	79.1	75.1	74.8	73.1	72.1	68.5
<b>P1N</b>	129.4	124.3	120.5	119.8	118.1	119.8	115.4
<b>C1N</b>	157.1	151.0	148.5	148.3	144.8	145.7	137.5
<b>C2N</b>	113.8	111.3	107.0	106.8	105.3	105.3	100.5
<b>T2N</b>	176.9	160.8	159.1	158.3	155.3	153.2	147.0

<sup>a</sup> Single point calculations on MP2/6-31G\* geometries.

**Table 3** The relative energies (kcal mol<sup>-1</sup>) of the valence isomers of phosphinine obtained at various levels of theory. Best estimates obtained using eqn. (1) are also given. Total energies, given in parenthesis, are in hartrees

Structure	HF/6-31G*	B3LYP/6-31G*	MP2/6-31G*	MP2/6-31G**	MP2/6-311+G** <sup>a</sup>	CCSD(T)/6-31G* <sup>a</sup>	Best estimate
<b>B1P</b>	0.0 (-532.95481)	0.0 (-534.87799)	0.0 (-533.69541)	0.0 (-533.73541)	0.0 (-533.82970)	0.0 (-533.77075)	0.0
<b>V1P</b>	53.2	50.6	44.0	43.9	41.9	45.2	42.0
<b>V2P</b>	56.8	57.5	52.2	52.0	50.3	52.7	49.1
<b>V3P</b>	69.6	67.6	60.0	59.8	59.1	61.2	58.8
<b>D1P</b>	59.1	59.6	58.4	58.2	56.3	55.7	52.0
<b>D2P</b>	70.3	67.7	63.6	63.6	62.3	61.3	58.7
<b>P1P</b>	93.8	91.6	87.4	87.0	85.5	87.7	84.3
<b>C1P</b>	108.2	108.2	108.3	108.4	105.5	105.8	99.4
<b>C2P</b>	107.4	102.3	98.3	98.2	96.9	97.4	93.4
<b>T2P</b>	146.8	133.5	132.3	131.6	128.9	126.7	121.8

<sup>a</sup> Single point calculations on MP2/6-31G\* geometries.

**Table 4** The relative energies (kcal mol<sup>-1</sup>) of the valence isomers of arsabenzene obtained at various levels of theory. Best estimates obtained using eqn. (1) are also given. Total energies, given in parenthesis, are in hartrees

Structure	HF/6-31G*	B3LYP/6-31G*	MP2/6-31G*	MP2/6-31G**	MP2/6-311+G** <sup>a</sup>	CCSD(T)/6-31G* <sup>a</sup>	Best estimate
<b>B1As</b>	0.0 (-2424.21413)	0.0 (-2427.27881)	0.0 (-2424.95069)	0.0 (-2424.99105)	0.0 (-2427.23077)	0.0 (-2425.02349)	0.0
<b>V1As</b>	46.3	43.4	37.3	37.1	35.9	38.3	35.9
<b>V2As</b>	52.8	53.1	48.1	47.9	48.0	48.5	46.7
<b>V3As</b>	68.1	65.8	58.0	57.8	57.7	59.0	57.2
<b>D1As</b>	53.5	54.2	52.7	52.5	53.4	49.6	48.5
<b>D2As</b>	67.2	64.5	60.1	60.0	59.2	57.6	55.3
<b>P1As</b>	87.1	84.2	79.9	79.6	80.5	80.0	79.0
<b>C1As</b>	105.3	104.7	104.7	104.9	103.9	101.9	97.4
<b>C2As</b>	106.8	100.9	95.8	95.7	93.2	95.0	89.8
<b>T2As</b>	139.1	126.3	124.3	123.6	120.9	118.4	113.3

<sup>a</sup> Single point calculations on MP2/6-31G\* geometries.

difference between the energies of the most stable and the least stable isomer decreases when going from the benzene family to the pyridine family, being 147.0 kcal mol<sup>-1</sup>. This difference further decreases to a greater extent for the valence isomers of phosphinine (121.8 kcal mol<sup>-1</sup>) and reduces a little for the valence isomers of arsabenzene (113.3 kcal mol<sup>-1</sup>) (Tables 2, 3 and 4). In all the classes of compounds considered here the benzene isomer (**B1X**) is computed to be the most stable and the *trans*-Dewar benzene isomer (**T2X**) to be the least stable isomer. The valence isomers of phosphinine follow the same relative energy ordering as those of arsabenzene. Absolutely no crossover in the relative energy orderings is found in going from the

valence isomers of phosphinine to arsabenzene (Fig. 8). Although the framework is chiefly responsible for the relative stabilities of the substituted valence isomers, the energy perturbations by skeletal substitutions are substantial among the benzvalene isomers. **V3N**, where the nitrogen is at the sp<sup>2</sup> center, is the most stable among the azabenzvalenes whereas the corresponding P/As substituted isomer, **V3P/V3As**, is the least stable. Similarly, in the case of Dewar benzene, the stability ordering of **D1X** and **D2X** is reversed when we go from X=N to P or N to As. In contrast, for the 3,3'-bicyclopropenyl isomers, a reversal in stability is not seen between **C1X** and **C2X** when going from X=N to P or As. But, the energy difference between

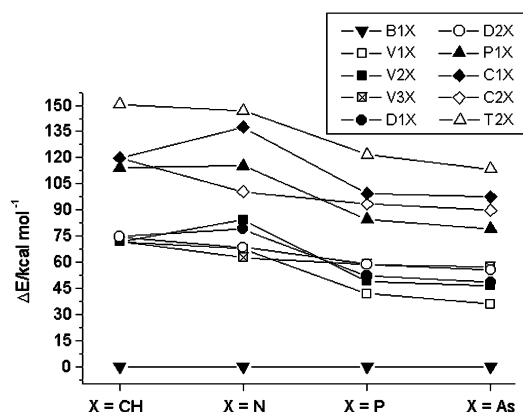


Fig. 8 The plot of the best estimates of the relative energies of the valence isomers of benzene and of group V heterobenzenes.

C1X and C2X for X=N is 37.0 kcal mol<sup>-1</sup>, while it is only 6.0 and 7.6 kcal mol<sup>-1</sup> for X=P and As, respectively. The N substitution always prefer to occupy the sp<sup>2</sup> center compared to the sp<sup>3</sup> one, as is evident from the higher stability of V3N, D2N and C2N compared to their other positional isomers. In contrast, the P and As substitutions prefer the sp<sup>3</sup> centers in benzvalene and Dewar benzene isomers. However, in the bicyclopropenyl isomers, the sp<sup>2</sup> center substituted isomers are marginally more stable. The relative energy orderings of the phosphinine and arsa-benzene valence isomers are identical and the energy gap between various isomers decreases slightly in going from the former to the latter.

## Conclusions

*Ab initio* and DFT calculations confirm that all the valence isomers of (CH)<sub>5</sub>X (X=N, P and As) are minima on their respective potential energy surfaces. The planar benzene analog is the lowest energy isomer in all cases and the relative energy ordering of the various classes of positional isomers resembles that of benzene in most cases. However, C2N is more stable than P1N. The range of energy gaps computed between various isomers and the energy range is substantially reduced for the heavier analogs. The relative energies obtained with the MP2 method are in consistently better agreement with coupled cluster calculations compared to those obtained at the HF or B3LYP levels. The hybrid density functional B3LYP method substantially overestimates the stability of the planar structures with delocalized  $\pi$  systems. The geometries obtained at the MP2 and the B3LYP levels are very similar in most cases and are in good agreement with the available experimental results. These studies reveal the richness of the valence isomers of group V hetero analogs of benzene. The success witnessed in the synthesis of phosphinine valence isomers should trigger synthetic attempts towards their aza and arsa analogs and these valence isomers have the potential to display intriguing isomerization reactions.

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