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Why Are $[P(C_6H_5)_4]^+N_3^-$ and $[As(C_6H_5)_4]^+N_3^-$ Ionic Salts and $Sb(C_6H_5)_4N_3$ and $Bi(C_6H_5)_4N_3$ Covalent Solids? A Theoretical Study Provides an Unexpected Answer[†]

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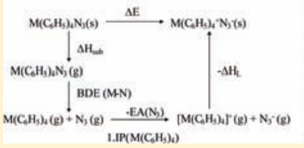
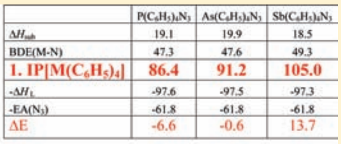
S *Supporting Information*

ABSTRACT: A recent crystallographic study has shown that, in the solid state, $P(C_6H_5)_4N_3$ and $As(C_6H_5)_4N_3$ have ionic $[M(C_6H_5)_4]^+N_3^-$-type structures, whereas $Sb(C_6H_5)_4N_3$ exists as a pentacoordinated covalent solid. Using the results from density functional theory, lattice energy (VBT) calculations, sublimation energy estimates, and Born−Fajans−Haber cycles, it is shown that the maximum coordination numbers of the central atom M, the lattice energies of the ionic solids, and the sublimation energies of the covalent solids have no or little influence on the nature of the solids. Unexpectedly, the main factor determining whether the covalent or ionic structures are energetically favored is the first ionization potential of $[M(C_6H_5)_4]$. The calculations show that at ambient temperature the ionic structure is favored for $P(C_6H_5)_4N_3$ and the covalent structures are favored for $Sb(C_6H_5)_4N_3$ and $Bi(C_6H_5)_4N_3$, while $As(C_6H_5)_4N_3$ presents a borderline case.





	$P(C_6H_5)_4N_3$	$As(C_6H_5)_4N_3$	$Sb(C_6H_5)_4N_3$
ΔH_{sub}	19.1	19.9	18.5
BDE(M-N)	47.3	47.6	49.3
1. IP[$M(C_6H_5)_4$]	**86.4**	**91.2**	**105.0**
$-\Delta H_L$	-97.6	-97.5	-97.3
-EA(N_3)	-61.8	-61.8	-61.8
ΔE	-6.6	-0.6	13.7

■ INTRODUCTION

Numerous examples are known where molecules are covalent in the gas phase, while in the solid state, they have ionic structures.[1−3] Typical examples are PCl_5, N_2O_5, Cl_2O_6, or FNO. The energy difference, ΔE, between the ionic solid and the covalent gas can be determined by a simple Born−Fajans−Haber cycle, as shown for FNO in Scheme 1. This energy difference is given by the sum of the bond dissociation energy [BDE(ON−F)] of the covalent gas when it separates into two free-radical fragments, the electron affinity [EA(F)] of the more electronegative fragment, the first ionization potential [1.IP(NO)] of the more electropositive fragment, and the lattice enthalpy term, $-\Delta H_L$, obtained by the appropriate correction of the lattice energy, $-U_L$, released when the resulting anion and cation form the ionic solid; so, $\Delta E = \mathrm{BDE(ON-F)} - \mathrm{EA(F)} + 1.\mathrm{IP(NO)} - \Delta H_L$.

The cases where closely related molecules can exhibit in their solid state either ionic or covalent structures are much less common and are not as well understood. It is commonly assumed that the governing factors in such cases are the maximum coordination numbers of the central atoms and the lattice and sublimation energies. To test the validity of these assumptions in a quantitative manner, we have selected the $M(C_6H_5)_4N_3$ series, where M = P, As, Sb, and Bi. A recent crystallographic and vibrational spectroscopic study[4] has shown that, in the solid state, the phosphorus and arsenic compounds are ionic $[M(C_6H_5)_4]^+N_3^-$ salts, whereas the antimony compound is a pentacoordinated covalent solid. Therefore, this series offered an excellent opportunity for analysis using a Born−Fajans−Haber cycle similar to the one shown in Scheme 1 but adapted to this special case by adding the sublimation enthalpy, ΔH_{sub}, of the covalent solid to the covalent gas-phase molecule (Scheme 2).

The calculations of the sublimation energies of the covalent solid to the covalent gas, the total energies of the covalent gas and the free gaseous ions, and the lattice energies allow the prediction of the energy differences, ΔE, between the covalent and ionic solids. Thermodynamically, ΔE is the important magnitude in the covalent−ionic isomerism reaction in Scheme 2 because the entropy change, ΔS, can be anticipated to be extremely small; the corresponding enthalpy change, ΔH ($\Delta H = \Delta E + P\Delta V$) will be approximately equal in magnitude to that of ΔE, which will also mirror the overall value of the Gibbs energy change, ΔG, for the target reaction above. For the phosphorus and arsenic compounds, the crystal structure data show that ΔE should be negative and, for the antimony compound, positive. Furthermore, this analysis provides insight into which intrinsic

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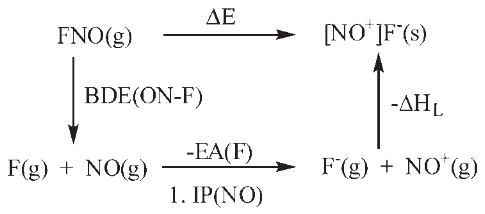
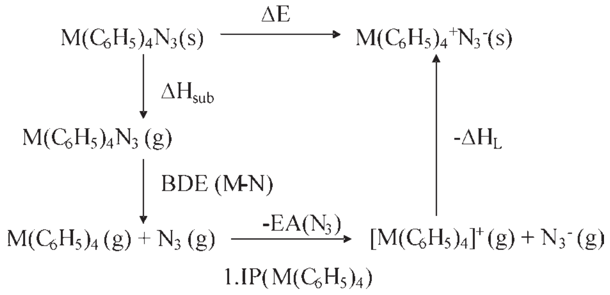
Scheme 1



Scheme 2



properties of these molecules are responsible for the change from ionic to covalent structures.

■ THEORETICAL METHODS

Density Functional Theory (DFT) Calculations. The initial structures and harmonic vibrational frequencies of covalent $M(C_6H_5)_4N_3$, where M = P, As, Sb, and Bi, of the corresponding cations $[M(C_6H_5)_4]^+$, and of the azide anion $[N_3]^-$ were optimized using the B3LYP[5] hybrid functional and the Stevens–Basch–Krauss–Jasien–Cundari effective core potential and valence-only basis set,[6] augmented with a spherical harmonic d-polarization function[7] and a diffuse s+p shell[8] on each heavy atom. A polar-coordinate grid with 96 radial, 36 θ, and 72 φ grid points was used with the *GAMESS* quantum chemistry package.[9] These geometries were reoptimized with the B3LYP functional and the following basis sets: C, H, and N, DZVP2;[10] P, aug-cc-pVDZ;[11] As, Sb, and Bi, aug-cc-pVDZ-PP.[12] We abbreviate this basis set combination as DZVP2 + aVDZ-PP. The heavy element calculations were done with small-core effective core potentials and correlation-consistent basis sets developed by the Peterson and Stuttgart groups. These calculations were done with the *Gaussian03* program system.[13]

Lattice Energy Calculations. Lattice energies, $-U_L$, were estimated using the VBT approach,[14] which related the lattice energy, U_L, to the ionic strength, I, of the lattice and the inverse cube root of the formula unit volume, V_m. This, in turn, is related to V_{cell}/Z where V_{cell} is the volume of the crystal unit cell and Z is the number of molecules per unit cell. The expression for the lattice energy is

$$U_L = 2I(\alpha V_m^{-1/3} + \beta) \qquad (1)$$

where α = 28.0 kcal·nm/mol and β = 12.4 kcal/mol. The data to calculate V_m for our target salts can be taken from Table 1 of ref 4, noting that for the $[As(C_6H_5)_4]N_3$ monohydrate it was necessary to subtract the volume of the hydrated water molecule prior to calculating the lattice energy of the anhydrous parent salt. We also calculated the volumes of the anion N_3^- and the cations at the B3LYP/DZVP2 + aVDZ+PP level using the 0.001 au contour.

Sublimation Energy Calculations. The B3LYP/DZVP2 + aVDZ-PP optimized geometries were subsequently used in single-point calculations to predict the boiling points using the COSMO-RS formalism,[15] as implemented in the *ADF* program.[16,17] The DFT densities in *ADF* for the COSMO-RS calculations of the boiling points were generated at the BP/QZ4P level.[18,19] The rule of Pictet and Trouton[20] with $\Delta H_{vap} = T_{BP}\Delta S$ (ΔG of a phase change = 0), where T_{BP} is the calculated boiling point and ΔS = 25 cal/mol·K was used to predict ΔH_{vap}. The value of 25 cal/mol·K was taken from our comparison of the boiling points of a range of substituted compounds.[21] The radii used for P, As, Sb, and Bi are 2.12, 2.16, 2.43, and 2.44 Å, respectively. The heat of melting of a wide range of compounds is 3 ± 2 kcal/mol, so we estimated ΔH_{sub} by adding 3 kcal/mol to the calculated ΔH_{vap}.[22]

■ RESULTS AND DISCUSSION

DFT Calculations. Because of the relatively large size of the molecules of this study, DFT was used for these calculations. As expected from the established maximum coordination numbers of 6 for P^V and As^{V1-3} and of 7 for Sb^V,[23] the P, As, and Sb central atoms should have no problems in accommodating four phenyl and one azido ligands in covalent, pentacoordinated, pseudo-trigonal-bipyramidal structures. In accordance with simple VSEPR arguments,[24] the more electronegative azido ligand should occupy one of the axial positions. These predictions were confirmed for the pentacoordinated covalent structures by our theoretical calculations, which showed vibrationally stable minimum-energy structures (see Table S1-1–4 of the Supporting Information).

For $P(C_6H_5)_4N_3$, a C_1 symmetry structure was predicted with a P–N bond length of 2.185 Å. Although this bond length is considerably longer than that of 1.79 Å, predicted for the P–N bond in $[NP(N_3)_2]_3$[25] and the sum of the covalent radii of P and N of 1.80 Å,[26] it is much shorter than the sum of the van der Waals radii of about 3.35 Å,[27] suggesting the presence of a covalent azido ligand with strong ionic contributions increasing the P–N bond length. The presence of strong ionic contributions is also reflected by the decreased difference of 0.05 Å between the N_α–N_β and N_β–N_γ bonds of the azido ligand. To investigate whether this lengthening of the P–N bond can be attributed to the influence of the four phenyl ligands, we have also calculated for comparison the structure of $P(CH_3)_4N_3$. For this molecule, three minimum-energy structures were predicted that differ only by less than 1.5 kcal/mol. The lowest-energy structure has C_s symmetry with a P–N bond length of 2.264 Å, somewhat longer than that of 2.185 Å, predicted for $P(C_6H_5)_4N_3$. Thus, the long P–N bond in $P(C_6H_5)_4N_3$ cannot be attributed to the steric influence of the phenyl groups. The other two minimum-energy structures of $P(CH_3)_4N_3$ were predicted to have P–N bond lengths of 3.13 and 3.31 Å, respectively, approaching the value of 3.35 Å for the sum of the van der Waals radii,[27] and, therefore, represent ion pairs.

For covalent $As(C_6H_5)_4N_3$ and $Sb(C_6H_5)_4N_3$, minimum-energy structures with M–N bond lengths of 2.308 and 2.266 Å, respectively, were predicted, 0.08–0.12 Å longer than those in $P(C_6H_5)_4N_3$. The main features of the predicted geometry of $Sb(C_6H_5)_4N_3$ agree well with those found in the crystal structure.[4]

As expected, DFT slightly overestimates most of the bond lengths, except for the Sb−N bond, where the predicted value of 2.266 Å is significantly shorter than the experimental value of 2.373 Å. This implies that in the experimental structure the N_3 ligand is somewhat more ionic than predicted. Further support for the increased ionicity of the azido group in the experimental structure comes from the fact that the observed difference of 0.048 Å between the $N_\alpha-N_\beta$ and the $N_\beta-N_\gamma$ bond lengths[4] is shorter than the predicted value of 0.062 Å. For covalent $P(CH_3)_4N_3$ and $As(CH_3)_4N_3$, a comparison of the predicted and experimental geometries is not possible because of the lack of experimental covalent structures.

The geometries predicted for the free $M(C_6H_5)_4^+$ (M = As, P) and N_3^- ions are in good agreement with the experimental results,[28] with the predicted bond lengths being about 0.02 Å longer than the experimental ones, as expected for DFT. Our results clearly demonstrate that in the covalent $M(CH_3)_4N_3$ molecules the maximum coordination numbers of the central atoms are not reached or exceeded and, thus, do not play a role in determining whether the preferred structures are ionic or covalent.

Of the required thermodynamic values, only the electron affinity of N_3 is known from the experiment,[29] 2.68 ± 0.03 eV (−61.8 kcal/mol), and this is the value used in our thermodynamic cycle calculations. For comparison, our calculated value for $EA(N_3)$ at the B3LYP/DZVP2 level is 59.5 kcal/mol. From the differences between the calculated total energies of the free gaseous $[M(C_6H_5)_4]^+$ and N_3^- ions and the free gaseous covalent $M(CH_3)_4N_3$ molecules and a knowledge of the sublimation energies and the electron affinity of N_3, the sum of the M−N BDE and 1.IP of $M(C_6H_5)_4$ can be obtained. In order to be able to split this sum into its two components, the covalent $M(C_6H_5)_4-N_3$ BDE and 1.IP of $M(C_6H_5)_4$ were calculated at the B3LYP/DZVP1 + aVDZ-PP level and are given in Table 1.

Lattice Energy Calculations. On the basis of the structure refinement data reported in Table 1 of ref 4, the formula unit volumes, V_m (calculated from V_{cell}/Z), are $V_m[P(C_6H_5)_4N_3] = 0.9876/2 = 0.4938\ nm^3$ and $V_m[As(C_6H_5)_4N_3 \cdot H_2O] = 2.2221/4 = 0.5555\ nm^3$ and using the thermodynamic difference rule[14c] $V_m[As(C_6H_5)_4N_3] = V_m[As(C_6H_5)_4N_3.H_2O] - V_m(H_2O)^6 = 0.5555 - 0.0245 = 0.531\ nm^3$ and $V_m[Sb(C_6H_5)_4N_3] = 2.0415/4 = 0.5104\ nm^3$. The calculated volumes are 0.4793 (P), 0.4851 (As), 0.4756 (Sb), and 0.5033 (Bi) nm^3 using a value of 0.0575 nm^3 for $V(N_3^-)$ (Table SI-3 in the Supporting Information). The calculated volumes are in reasonable agreement with the experimental values. Taking the lattice ionic strength, I, to be 1, the lattice energies can be calculated. These can be corrected to lattice enthalpies, ΔH_L, using the correction procedure described previously[14e] ($\Delta H_L = U_L + 2RT$), where $2RT = 1.2$ kcal/mol at 298 K.

Table 1. Components of the Born−Fajans−Haber Cycles of Scheme 2 and Energy Differences, ΔE, between the Covalent and Ionic Solids for $M(C_6H_5)_4N_3$ (M = P, As, Sb, Bi) in kcal/mol

	$P(C_6H_5)_4N_3$	$As(C_6H_5)_4N_3$	$Sb(C_6H_5)_4N_3$	$Bi(C_6H_5)_4N_3$
ΔH_{sub}	19.1	19.9	18.5	20.3
BDE(M−N)	47.3	47.6	49.3	33.6
1. IP$[M(C_6H_5)_4]$	86.4	91.2	105.0	119.2
$-\Delta H_L$	−97.6	−97.5	−97.3	−96.2
$-EA(N_3)$	−61.8	−61.8	−61.8	−61.8
ΔE	−6.6	−0.6	13.7	15.1

Sublimation Energy Calculations. The calculated boiling points for $M(C_6H_5)_4N_3$ are 643 K (P), 675 K (As), 620 K (Sb), and 693 K (Bi). The boiling points lead to predicted ΔH_{vap} values of 16.1 (P), 16.9 (As), 15.5 (Sb), and 17.3 (Bi) kcal/mol, which lead to the estimated ΔH_{sub} values in Table 1. The small variation in the calculated sublimation enthalpies on going from $P(C_6H_5)_4N_3$ to $Bi(C_6H_5)_4N_3$ is supported by the very small variations experimentally found for the closely related series SF_6 (5.54 ± 0.003 kcal/mol), SeF_6 (5.96 ± 0.01 kcal/mol), and TeF_6 (6.12 kcal/mol).[30]

Born−Fajans−Haber Cycles. The results from the Born−Fajans−Haber cycles for Scheme 2 are summarized in Table 1. The sublimation energies, the lattice enthalpies, and $EA(N_3)$ are approximately constant. For P, As, and Sb, the $M-N_3$ BDEs are also approximately constant, so it is the value of 1.IP of $M(C_6H_5)_4$ that determines whether these $M(CH_3)_4N_3$ compounds are ionic or covalent. The constant values for the $M-N_3$ BDEs for P, As, and Sb suggest that there is some steric ligand effect compensating for the expected decrease in the BDE with an increase in the atomic number, as shown by the fact that in $P(CH_3)_4N_3$ the BDE is not coupled with the long P−N bond.

For these molecules, the 1.IP of $M(C_6H_5)_4$ increases with an increase in the atomic number of the central atom. $P(C_6H_5)_4$ has the lowest ionization potential (IP) because it most readily gives up its electron to form the corresponding cation, leading to an ionic solid. $As(C_6H_5)_4N_3$ is right at the border between covalent and ionic behavior, with 1.IP of $As(C_6H_5)_4$ being about 5 kcal/mol higher than that of $P(C_6H_5)_4$. The value of 1.IP substantially increases by 14 kcal/mol from $As(C_6H_5)_4$ to $Sb(C_6H_5)_4$, so $Sb(C_6H_5)_4N_3$ is a covalent solid. Although there is a substantial decrease in the $M-N_3$ BDE for Bi, it is compensated for by a substantial increase in 1.IP of $Bi(C_6H_5)_4$, so $Bi(C_6H_5)_4N_3$ is predicted to be also an ionic solid with an ionic−covalent energy difference similar to that of $Sb(C_6H_5)_4N_3$. Thus, the results from our Born−Fajans−Haber cycles confirm that $P(C_6H_5)_4N_3$ should be ionic and $Sb(C_6H_5)_4N_3$ and $Bi(C_6H_5)_4N_3$ should be covalent by relatively large margins of ΔE, while $As(C_6H_5)_4N_3$ represents a borderline case.

It should be noted that 1.IPs of the $M(C_6H_5)_4$ radicals do not follow the periodic trend of the central atoms (Table 2), which is

Table 2. Nonperiodic Behavior of Molecular IPs in eV

M	atom expt[32]	MF_3 expt	MF_3 calc	MCl_3 expt	MCl_3 calc
N	14.53414	12.94 ± 0.01[32]	12.60	10.1 ± 0.1[33c]	9.77
P	10.48669	11.38 ± 0.10[32]	11.87	9.90 ± 0.01[32]	10.03
As	9.8152	12.84 ± 0.05[33b] 12.3 ± 0.05[33a]	12.53	10.55 ± 0.025[31,33d]	10.41
Sb	8.64	12.1[31]	12.16	10.1 ± 0.1[31]	10.41
Bi	7.2855		12.37	10.4[31]	10.63

decreasing with an increase in the atomic number, and, in fact, exhibit the opposite trend. This arises because of the different stabilities in the neutral radical and in the cation. Nonperiodic behavior is shown in the calculated and experimental IPs of the MF_3 compounds, as shown in Table 2[31−33] In addition, the IPs of the MCl_3 compounds exhibit a trend similar to that of $M(C_6H_5)_4$ of increasing IP with an increase in the atomic number. Thus, atomic correlations can be very different from molecular correlations. The calculations in Table 2 were done at the same level as those for the $M(C_6H_5)_4$ compounds.

CONCLUSION

Our study surprisingly shows that, contrary to intuition, the value of 1.IP of $M(C_6H_5)_4$ determines whether these $M(CH_3)_4N_3$ compounds are ionic or covalent. In agreement with the known crystal structures, $P(C_6H_5)_4N_3$ is found to be ionic and $Sb(C_6H_5)_4N_3$ is predicted to be covalent, while $As(C_6H_5)_4N_3$ represents a borderline case.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Calculated geometries for $[M(C_6H_5)_4]^+N_3^-$ compounds at the B3LYP/DZVP2 + aVDZ-PP level (Table SI-1), calculated frequencies (cm^{-1}) for $[M(C_6H_5)_4]^+N_3^-$ compounds at the B3LYP/DZVP2 + aVDZ-PP level (Table SI-2) with IR intensities (km/mol) and Raman intensities ($Å^4$/amu), calculated volumes (nm^3/molecule) for $[M(C_6H_5)_4]^+N_3^-$ compounds at the B3LYP/DZVP2 + aVDZ-PP level (Table SI-3), and calculated total energies (au) for $[M(C_6H_5)_4]^+N_3^-$ compounds at the B3LYP/DZVP2 + aVDZ-PP level (Table SI-4). This material is available free of charge via the Internet at http://pubs.acs.org.

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DEDICATION

[†]Dedicated to Professor Herbert W. Roesky on the occasion of his 75th birthday.

REFERENCES

(1) *Holleman−Wiberg's Inorganic Chemistry*; Academic Press: San Diego, CA, 2001.

(2) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, 2nd ed.; Butterworth-Heinemann: Oxford, U.K., 1998.

(3) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley and Sons, Inc.: New York, 1999.

(4) Haiges, R.; Schroer, T.; Yousufuddin, M.; Christe, K. O. *Z. Anorg. Allg. Chem.* **2005**, *631*, 2691.

(5) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5642. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623–11627. Hertwig, R. H.; Kock, W. *Chem. Phys. Lett.* **1997**, *268*, 345–351.

(6) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6026–6033. Stevens, W. J.; Krauss, M.; Basch, H.; Jasien, P. G. *Can. J. Chem.* **1992**, *70*, 612–630. Cundari, T. R.; Stevens, W. J. *J. Chem. Phys.* **1993**, *98*, 5555–5565.

(7) The d-polarization function exponents used were 0.8 (C and N), 0.55 (P), 0.293 (As), and 0.211 (Sb).

(8) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294–301.

(9) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347–1363.Gordon, M. S.; Schmidt, M. W. In *Theory and Applications of Computational Chemistry: the First Forty Years*; Dykstra, C. E., Frenking, G., Kim, K. S., Scuseria, G. E., Eds.; Elsevier: Amsterdam, The Netherlands, 2005; pp 1167−1189.

(10) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560–571.

(11) (a) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007. (b) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(12) Metz, H.; Stoll, M.; Dolg, J. *J. Chem. Phys.* **2000**, *113*, 2563–2569. Peterson, K. A. *J. Chem. Phys.* **2003**, *119*, 11099–11112.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuna, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowshi, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(14) (a) Glasser, L.; Jenkins, H. D. B. *Chem. Soc. Rev.* **2005**, *34*, 866. (b) Jenkins, H. D. B.; Roobottom, H. K.; Passmore, J.; Glasser, L. *Inorg. Chem.* **1999**, *38*, 3609. (c) Jenkins, H. D. B.; Glasser, L. *J. Am. Chem. Soc.* **2004**, *126*, 15809. (d) Jenkins, H. D. B.; Glasser, L. *Inorg. Chem.* **2002**, *41*, 4378.(e) Jenkins, H. D. B. *J. Chem. Educ.* **2005**, *82*, 950. (f) Glasser, L.; Jenkins, H. D. B. *J. Chem. Eng. Data* **2010**10.1021/je100683u.

(15) Klamt, C. A. *J. Phys. Chem.* **1995**, *99*, 2224.Klamt, C. A. *Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design*; Elsevier: Amsterdam, The Netherlands, 2005. Klamt, C. A.; Jonas, V.; Burger, T.; Lohrenz, J. C. *J. Phys. Chem. A* **1998**, *102*, 5074.

(16) Baerends, E. J.; Austchbach, J.; Berces, A.; Bickelhaupt, F. M.; Bo, C.; Boerrigter, P. M.; Cavallo, L.; Chong, D. P.; L., D.; Dickson, R. M.; Ellis, D. E.; van Faassen, M.; Fan, L.; Fischer, T. H.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Gotz, A. W.; Groeneveld, J. A.; Gritsenko, O. V.; Gruning, M.; Harris, F. E.; van den Hoek, P.; Jacob, C. R.; Jacobsen, H.; Jensen, L.; van Kessel, G.; Kootstra, F.; Krykunov, M. V.; van Lenthe, E.; McCormack, D. A.; Michalak, A.; Neugebauer, J.; Nicu, V. P.; Osinga, V. P.; Patchkovskii, S.; Philipsen, P. H. T.; Post, D.; Pye, C. C.; Ravenek, W.; Rodriguez, J. I.; Ros, P.; Schipper, P. R. T.;

Schreckenbach, G.; Snijders, J. G.; Sola, M.; Swart, M.; Swerhone, D.; te Velde, G.; Vernooijs, P.; Versluis, L.; Visscher, L.; Visser, O.; Wang, F.; Wesolowski, T. A.; van Wezenbeek, E. M.; Wiesenekker, G.; Wolff, S. K.; Woo, T. K.; Yakovlev, A. L.; Ziegler, T. *ADF2008.01*; SCM: Amsterdam, The Netherlands, 2008.

(17) Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 391. te Velde, G.; Bickelhaupt, F. M.; van Gisbergen, S. J. A.; Fonseca Guerra, C.; Baerends, E. J.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931–967.

(18) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(19) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822. Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7406.

(20) Pictet, R. G. *Ann. Chem. Phys.* **1876**, *183*, 180. Trouton, F. *Philos. Mag.* **1884**, *18*, 54. Hildebrand, J. H. *J. Am. Chem. Soc.* **1915**, *37*, 970.Lewis, G. N. *Thermodynamics*; McCraw Hill: New York, 1961. Waser, J. *Basic Chemical Thermodynamics*; W. A. Benjamin: New York, 1966.

(21) Davis, B. L.; Dixon, D. A.; Garner, E. B.; Gordon, J. C.; Matus, M. H.; Stephens, F. H. *Angew. Chem.* **2009**, *48*, 6812.

(22) Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*, 86th ed.; Taylor and Francis: Boca Raton, FL, 2005.

(23) Drake, G. W.; Dixon, D. A.; Sheehy, J. A.; Boatz, J. A.; Christe, K. O. *J. Am. Chem. Soc.* **1998**, *120*, 8392.

(24) Gillespie, R. J.; Hargittai, I. *The VSEPR Model of Molecular Geometry*; Allyn and Bacon: Boston, 1991.

(25) Tornieporth-Oetting, I. C.; Klapoetke, T. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 511.

(26) Klapoetke, T. M.; Tornieporth-Oetting, I. C. *Nichtmetallchemie*; VCH: Weinheim, Germany, 1994.

(27) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(28) The previously published crystal structure for $[As(C_6H_5)_4]^+N_3^-$ (Crawford, M.-J.; Klapoetke, T. M. *Heteroatom Chem.* **1999**, *10*, 325) suffered from the small size of the selected crystals and a low R factor of 13%, resulting in an average As−C bond length of 1.89 Å. Our more accurate crystal structure of $[As(C_6H_5)_4]^+N_3^- \cdot H_2O$ gives a value of 1.911 Å for the As−C distance, which is in much better agreement with our theoretical predictions.

(29) Yang, X.; Kiran, B.; Wang, X. B.; Wang, L. S.; Mucha, M.; Jungwirth, P. *J. Phys. Chem. A* **2004**, *108*, 7820.

(30) Chicos, J. S.; Acree, W. E., Jr. *J. Phys. Chem. Ref. Data* **2002**, *31*, 2002.

(31) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Supplement 1.

(32) NIST Webbook, http://webbook.nist.gov/chemistry/.

(33) (a) Pabst, R. E.; Sharpe, M. C.; Margrave, J. L.; Franklin, J. L. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *33*, 187. (b) Muller, J.; Fenderl, K. *Chem. Ber.* **1971**, *104*, 2207. (c) Colbourne, D.; Frost, D. C.; McDowell, C. A.; Westwood, N. P. C. *J. Chem. Phys.* **1978**, *69*, 1078. (d) Johnstone, R. A. W.; Mellon, F. A. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1209.