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Electronic Structure of Binary Phosphoric and Arsenic Triazides

Zeng Xiaoqing,[a,b] Wang Weigang,[a,b] Liu Fengyi,[a] Ge Maofa,*[a] Sun Zheng,[a] and Wang Dianxun*[a]

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Two highly explosive binary triazides of the group 15 elements $P(N_3)_3$ and $As(N_3)_3$ have been obtained in the gas phase through the heterogeneous reaction of PCl_3 and $AsCl_3$, respectively with AgN_3 at room temperature. The electronic structures of both triazides have been characterized by photoelectron spectroscopy, combined with quantum chemical calculations. This represents the first electronic study of covalent triazides. The first experimental vertical ionization potentials for $P(N_3)_3$ and $As(N_3)_3$ are 9.74 and 9.98 eV, with the contribution primarily from the lone pairs of the azido moiety and the arsenic atom, respectively. The results indicate the relative "isolation" of azido moieties in triazides and less stability of these highly explosive compounds in comparison to monoazides and diazides.

Introduction

The first synthesis of a covalent azide HN_3 was reported by Curtius more than 100 years ago.[1] However, the chemistry of covalent azides received little attention until the early 1960s, presumably because of their explosive nature and shock sensitivity.[2] Especially the synthesis, isolation, and structural characterization of high-energy compounds are an experimental challenge for chemists.[3] Binary azides of group 15 elements belong to this class of compounds, and little is known about their synthesis, structure, and properties.[4] For nitrogen azides, most studies are focused on theoretical predictions, such as the structures and stabilities of the azidamines $N(N_3)_3$ and $HN(N_3)_2$, the $N(N_3)_2^-$ anion, and the $N(N_3)_4^+$ cation.[5] However, the successful synthesis of the novel N_5^+ cation[6] by Christe et al. has greatly encouraged more research on polynitrogen compounds.[7] The binary phosphorus azides $P(N_3)_3$, $P(N_3)_4^+$, $P(N_3)_5$, $P(N_3)_6^-$, and $N_5^+[P(N_3)_6]^-$ have been characterized by vibrational methods and ^{31}P NMR spectroscopy, but no structural information is available.[8,9] For arsenic azides, much research has been devoted to the preparation and characterization of these compounds:[10] the first preparation of $As(N_3)_3$ and $As(N_3)_4^+$ was reported by Klapötke et al. in 1995;[10a,10c] the crystal structure of $As(N_3)_3$ was determined by Christe et al. in 2004;[11] and the crystal structure of $As(N_3)_6^-$ was determined by Klapötke et al. in 2000.[10c]

[a] State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences,
Beijing, 100080, China
Fax: +86-10-62559373
E-mail: gemaofa@iccas.ac.cn
[b] Graduate School of Chinese Academy of Sciences,
Beijing, 100039, China
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The electronic and molecular structures of many azides (unstable molecules) have been studied with theoretical and spectroscopic methods.[12] Recently, photoelectron spectroscopy in combination with high-level quantum chemical calculations has been successfully performed for elucidating many interesting aspects of monoazides[13] and diazides.[14] The focus of these studies is the interaction taking place between the off-the-axis substituent group and the nearly linear N_3 moiety, as well as the interaction between the N_3 moieties. In 1994, Novak et al. studied the electronic structures of $(CF_3)_2AsN_3$ and $CF_3As(N_3)_2$.[15] However, reports on the electronic structure of triazide are rare because of their explosiveness. Herein, we report the experimental and calculated electronic structures of binary phosphorus and arsenic triazides.

Results and Discussion

Molecular Structures

Geometry optimizations were performed for $P(N_3)_3$ and $As(N_3)_3$ using the DFT method (B3LYP). All stationary points were verified as local minima by vibrational analysis. Three local minima were located for both triazides (see Figure 1 and Table 1). The relative energies for the stable conformers are listed in Table 2. Zero-point vibrational-energy corrections for these minima of $P(N_3)_3$ and $As(N_3)_3$ differ by less than 0.4 and 0.2 kcal mol^{-1}, respectively. The most stable structure at the B3LYP/6-311++G(3df) level is the conformer **b** with C_s symmetry, in which two azido ligands adopt an approximate *gauche* orientation relative to the stereochemically active lone pair on the P/As atom, with the remaining azido ligand in an *anti* orientation. For $P(N_3)_3$,

the calculated P–N bond length, 1.73–1.74 Å, is slightly shorter than a typical P–N single bond with 1.76 Å,[16] while longer than a typical P=N double bond with 1.55 Å in iminophosphane (HP=NH).[17] Meanwhile, the azido moiety lies in an almost planar environment with the central P atom (see Table 1); this may provide an opportunity for interactions between the lone pair on the P atom with the three azido ligands to stabilize this conformer. The second most stable conformer of phosphorus triazide, **a**, with C_3 symmetry, is 1.46 kcal mol^{-1} higher in energy than conformer **b** and has all three azido ligands in a *gauche* orientation. This energy gap may be the result of the interactions between the sterically active lone pair on the phosphorus atom and the three azido ligands. Finally, the least stable structure, **c** (C_3 symmetry), has all three azido ligands pointing away from the phosphorus lone-pair, and is 2.90 kcal mol^{-1} higher in energy than conformer **b**. This structure was calculated to be a real local minimum at the B3LYP/6-311++G(d) level of theory,[18] however, the distances between N2 and N2′, and N3 and N3′ are 3.38 and 4.37 Å, respectively, which are much shorter than those in conformer **a** (4.41 and 6.21 Å, respectively). Also, the natural atomic population (NAO)[19] net charges calculated for this conformer are Q_P = +1.11 e on phosphorus, Q_{N1} = –0.68 e on the adjacent nitrogen atom, Q_{N2} = +0.43 e on the second nitrogen atom, and Q_{N3} = –0.12 e on the last nitrogen atom, indicating that the interactions between N1 and N1′, N2 and N2′, as well as N3 and N3′ might decrease the stability of this conformer.

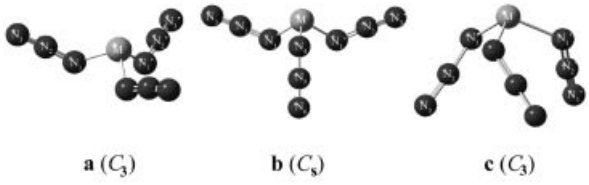

Figure 1. Local minima calculated for $M(N_3)_3$ (M = P, As) at the B3LYP/6-311++G(3df) level of theory. (The geometric parameters are given in Table 1.).

For $As(N_3)_3$, three similar stable conformers were located, with conformer **b** being the most stable structure. However, the most stable conformer previously reported by

Table 1. Calculated bond lengths [Å], bond angles [°], and torsion angles [°] for the local minima (**a**–**c**; see Figure 1) of $P(N_3)_3$ and $As(N_3)_3$ (given in parentheses) at B3LYP/6-311++G(3df) level.

Conformer **a** E[a] = +1.46 kcal mol^{-1} (2.06)		Conformer **b** E = 0.00 kcal mol^{-1} (0.00)	
M–N1	1.732 (1.884)	M–N1	1.740 (1.888)
N1–N2	1.229 (1.229)	N1–N2	1.229 (1.229)
N2–N3	1.125 (1.128)	N2–N3	1.126 (1.128)
		M–N4	1.730(1.889)
N1–M–N1′	96.5 (94.1)	N4–N5	1.234 (1.231)
N2–N1–M	119.3 (117.6)	N5–N6	1.123 (1.126)
N3–N2–N1	174.3 (174.5)		
N3–N2–N1–M	176.9 (179.1)	N1–M–N1′	91.8 (88.2)
N2–N1–M–N1′	106.2 (96.7)	N2–N1–M	119.2 (117.6)
Conformer **c** E = +2.90 kcal mol^{-1} (0.94)		N3–N2–N1	174.4(174.4)
		N1–M–N4	101.4(99.9)
M–N1	1.744 (1.898)	N5–N4–M	121.3 (119.0)
N1–N2	1.228 (1.228)	N6–N5–N4	175.4 (175.7)
N2–N3	1.125 (1.127)		
N1–M–N1′	101.8 (99.8)	N3–N2–N1–M	178.4 (178.1)
N2–N1–M	123.0 (120.1)	N2–N1–M–N1′	157.1 (166.7)
N3–N2–N1	175.8 (176.0)	N6–N5–N4–M	180.0 (180.0)
		N5–N4–M–N1	47.1 (45.0)
N3–N2–N1–M	155.6 (169.0)	N2–N1–M–N4	100.9 (99.5)
N2–N1–M–N1′	95.1 (94.0)		

[a] Relative energy including ZPE corrections.

Table 2. Total energies (hartree) of conformers of $P(N_3)_3$ at different levels of theory, relative energies (kcal/mol) at the B3LYP/6-311++G(3df) level of theory, and the values for $As(N_3)_3$ at the B3LYP/6-311++G(3df) level of theory are given in parentheses.

Conformer	B3LYP/6-31+G(d)	B3LYP/6-311++G(3df)	CCSD(T)/6-31G(d)	RE[a]
a	–833.9572663	–834.1622444 (–2728.6537522)	–832.1959352	1.46 (2.06)
b	–833.9601526	–834.1647579 (–2728.6572297)	–832.1995274	0.00 (0.00)
c	–833.9548009	–834.1596547 (–2728.6554279)	–832.1953666	2.09 (0.94)

[a] Relative energies with zero-point vibrational-energy corrections included.

using second-order perturbation theory (MP2), which had C_1 symmetry with two azido ligands adopting an *anti* orientation and the third azido ligand in a *gauche*-like orientation,[11] was calculated to be not a real local minimum at the B3LYP/6-311++G(3df) level of theory, and the relative energies for the two less stable conformers **a** and **c** here were calculated to be 2.06 and 0.94 kcal mol^{-1} higher than conformer **b**, including the zero-point energy (ZPE) corrections.

Photoelectron Spectroscopy

The He I photoelectron spectra of $P(N_3)_3$ and $As(N_3)_3$ are shown in Figure 2. Table 3 lists photoelectron spectroscopy (PES) experimental vertical ionization energies (IP in eV), theoretical vertical ionization energies (E_v in eV), molecular orbital symmetries, and characters of outer valence shells for the most stable conformers by OVGF calculations for both triazides. The ionization potentials calculated for the other two stable conformers are also included. Because the three conformers with comparable energies are possible in some cases, first we should investigate whether the spectra can originate from a mixture of all three conformers or some of them dominate. However, in comparison to the calculated orbital energies, we limit our discussions to the analysis of the slightly more stable C_s-conformer **b** for $P(N_3)_3$ and $As(N_3)_3$.

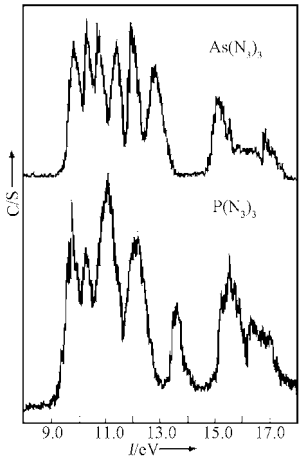

Figure 2. Full He I photoelectron spectra of $P(N_3)_3$ and $As(N_3)_3$.

P(N$_3$)$_3$

The photoelectron (PE) spectrum of $P(N_3)_3$ is much more complicated than that of HN_3,[20] owing to the participation of the phosphorus lone-pair. In the low ionization region (<15 eV) there are five bands with no obvious vibrational structure. From the calculated orbital characters shown in Table 3 and Figure 3, it can be easily concluded that all five bands originate from the removal of the lone pair on the phosphorus or the nitrogen atoms of the azido moieties. The first broad band centered at 9.74 eV matches well with the calculated value 9.81 eV, which is attributed to the ionization of lone pairs from the three azido moieties with almost equal contributions. Similar ionization processes also occur in other azides, such as CH_3N_3 (9.81 eV)[21] and $SO(N_3)_2$ (10.18 eV).[14] However, as we know, the removal of lone pair electrons or degenerate π orbital electrons leads to sharp peaks and lower ionization potentials in the PE spectrum of the molecule studied. This indicates that the peak caused by removing electrons from 25a′, with a calculated energy of 9.83 eV, overlaps with the peak caused by removing electrons from HOMO 14a′′. The calculated MO character of the second highest occupied orbital (SHOMO) 25a′ indicates that it has the dominant attribution from the P lone-pair (P3p) (Figure 3). The ionization of similar P lone-pairs actually happens in the low ionization region as well, such as PH_3 (10.59 eV)[22] and $(CH_3O)_3P$ (9.30 eV).[23] The second observed band with

Table 3. Experimental and calculated [ROVGF/6-311G(d)] ionization energies [eV].

$IE_{exp.}$	$IE_{calcd.}$			Assignment
$P(N_3)_3$	**a** (C_3)	**b** (C_s)	**c** (C_3)	
9.74	9.34	9.81	9.58	14a′′ LpN3 [a]
	10.14	9.83	10.44	25a′ P3p [b]
10.37	10.77	10.43	11.66	24a′ LpN3
11.08	10.77	10.79	12.38	13a′′ LpN3
	11.75	11.93	12.76	12a′′ $\pi_{P\text{-}N4}$, $\sigma_{P\text{-}N1}$, $\sigma_{P\text{-}N1'}$
12.17	11.75	12.19	16.07	23a′ $\pi_{N1\text{-}P\text{-}N1'}$, $\pi_{N5\text{-}N6}$
13.59	14.47	13.82	16.34	22a′ P3p
15.6	15.88	15.82	17.11	11a′′ $\sigma_{N1\text{-}N2\text{-}N3}$, $\sigma_{N1'\text{-}N2'\text{-}N3'}$
$As(N_3)_3$				
9.98	9.44	9.73	9.65	17a′′As4p [c]
		9.87		31a′ LpN3
10.22	10.28	10.18	10.11	30a′ As4p, LpN3
10.7	10.31	10.36	11.17	16a′′ LpN3
11.43	11.39	11.61	11.17	15a′′ $\pi_{As\text{-}N4}$, $\sigma_{As\text{-}N1}$, $\sigma_{As\text{-}N1'}$
11.91	14.49	11.72	11.88	29a′ $\pi_{N1\text{-}As\text{-}N1'}$, $\pi_{N5\text{-}N6}$
12.95	15.64	13.99	13.2	28a′ As4p
15.2	15.87	15.54	15.77	14a′′ $\sigma_{N1\text{-}N2\text{-}N3}$, $\sigma_{N1'\text{-}N2'\text{-}N3'}$

[a] Lp is the abbreviation of lone pair electrons. [b] 3p lone-pair on the phosphorus atom. [c] 4p lone-pair on the arsenious atom.

vertical ionization energy of 10.37 eV agrees well with the calculated value 10.43 eV for orbital 24a′, as can be seen in Figure 3; it has the character of nitrogen lone-pairs on the three azido moieties. The third kind of linear combination is embodied in the third broad band (11.08 eV), which ranges from 10.50 to 11.70 eV. Based on the calculated results and experimental intensity of this band, it is assigned to the removal of electrons from 13a′′ and 12a′′ orbitals. The π_{P-N4} formed by the interaction of P3p with the N4 lone-pair is also attributed. The fourth band with experimental vertical ionization energy of 12.17 eV, corresponding to the calculated 12.19 eV for 23a′, has the character $\pi_{N1-P-N1'}$, π_{N5-N6} (Figure 3). The next band with a vertical ionization of 13.59 eV corresponds to MO 22a′, which has the dominant character of the P3p lone-pairs. A similar band also occurs in PH_3 (13.6 eV).[22] The band centered near 15.6 eV in the high ionization region (>15.0 eV) is considered to be the ionization of electrons from several deep-shell orbitals in $P(N_3)_3$.

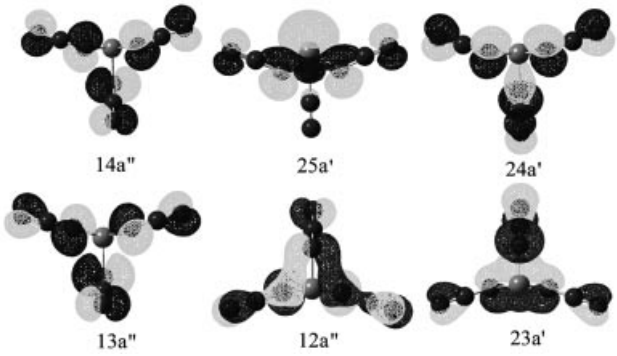

Figure 3. Characters of the six highest occupied molecular orbitals (HOMOs) of C_s: $P(N_3)_3$ (isovalue = 0.04).

As(N₃)₃

The electronic structures of two arsenic azides $(CF_3)_2AsN_3$ and $CF_3As(N_3)_2$ have been reported previously.[15] The main interest in the analysis was the interactions taking place between the off-the-axis substituent and the linear (or nearly so) azido group. It was concluded that the larger bandwidth in their PE spectra may signify greater delocalization and bonding interaction between the azido moieties and the rest of the molecule. Compared with the PE spectra of the two above-mentioned azides, the bands in the PE spectrum of $As(N_3)_3$ are clearer and narrower in the low ionization region (<15.0 eV). The calculated MO characters (Figure 4) of this triazide reveal that the lone pair electrons on the azido moieties are more pronounced than in the monoazide and diazide, and imply weaker azido–azido interactions. These weaker interactions also lead to the lower stability of triazide.

In the low ionization region (<15.0 eV), six bands are clearly displayed. Because of the electronic similarity of phosphorus and arsenic, most outer valence shells for $As(N_3)_3$ are similar to that of $P(N_3)_3$. However, the HOMO in arsenic triazide is primarily the attribution of the 4p lone-pair from the As atom (As4p). The vertical ionization potential is 9.98 eV, which is slightly smaller than that of $(CF_3)_2AsN_3$ (10.40 eV) and $CF_3As(N_3)_2$ (10.23 eV),[15] and it corresponds to the calculated 9.73 eV for conformer **b**. Similar to the first band in the PE spectrum of $P(N_3)_3$, the ionization of electrons in the SHOMO 31a′ also happens in this region, with the contribution of the lone pair on nitrogen atoms of the three azido moieties being calculated as 9.87 eV. The second band at 10.22 eV originates not only from the lone pair of the nitrogen atoms on the azido ligands, but also the As4p lone-pair. The third band at 10.70 eV mainly comes from the ionization of the 16a′′ LPN3 (azido lone-pair) electron, and the fourth band at 11.43 eV should be from the 15a′′ π_{As-N4}, σ_{As-N1}, $\sigma_{As-N1'}$ (see Figure 4). In $P(N_3)_3$, the bands caused by removal of electrons from these two orbitals overlap. The main characters for the remaining two bands at 11.61 and 12.95 eV are similar to those of $P(N_3)_3$ (Figure 4). In the high ionization region (>15.0 eV), there also exist several broad bands, ranging from 15.00 to 17.50 eV, which might be the ionization of electrons from inner molecular orbitals.

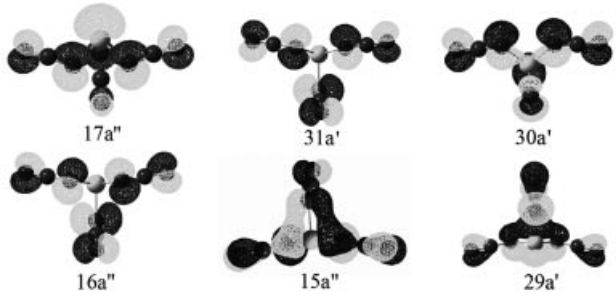

Figure 4. Characters of the six highest occupied molecular orbitals (HOMOs) of C_s: $As(N_3)_3$ (isovalue = 0.04).

Conclusions

The electronic structures of two similar triazides, $P(N_3)_3$ and $As(N_3)_3$, were studied by means of PES and ab initio calculations. Three stable conformers for $P(N_3)_3$ and $As(N_3)_3$ were located at the B3LYP/6-311++G(3df) level of theory. It was found that the conformer **b** with C_s symmetry is the most stable for both triazides. The first ionization potentials of these two stable conformers for $P(N_3)_3$ and $As(N_3)_3$ are 9.74 and 9.98 eV respectively, with the primary characters being the azido lone-pairs for $P(N_3)_3$ and the As4p lone-pairs for $As(N_3)_3$. The SHOMO for the two compounds mainly comes from the P3p lone-pair for $P(N_3)_3$, in comparison to the lone pairs of the azido group for $As(N_3)_3$. Another interesting aspect is that the PES bands for both triazides are almost all sharp without recognizable vibrational structure. And it is known that triazides are usually much less stable than the corresponding di- and mono- derivatives. The relative "isolation" of azido groups and less delocalization in triazides may account for this experimental fact.

Experiment and Calculation

Recently, many azide-containing compounds have been successfully prepared and characterized,[13,14] and it was found that AgN_3 is an ideal precursor for the in situ preparation of highly explosive azides through the heterogeneous reactions with reactive halogen-containing molecules. $P(N_3)_3$ and $As(N_3)_3$ were prepared in a similar manner by the heterogeneous reactions of gaseous PCl_3 and $AsCl_3$ with AgN_3 at low pressure (10^{-5} Torr). Both reactants were purchased from ACROS and distilled before the PES experiment, and their PE spectra were identical with those in the literature.[23,24] Solid AgN_3 was prepared as reported.[14] For efficient reaction, freshly prepared AgN_3 was loosely dispersed on the surface of quartz wool and filled the quartz inlet tube. After the vacuum reached 10^{-5} Torr, the vapor of the PCl_3 or $AsCl_3$ was passed through the solid AgN_3 at ambient temperature. The reactions [Equation (1) and Equation(2)] proceeded smoothly without the evolution of the possible decomposition product N_2. The He I PE spectra of $P(N_3)_3$ and $As(N_3)_3$ were recorded with a double-chamber machine[25] that was built specifically to detect transient species at a resolution of about 30 meV as indicated by the Ar^+ ($^2P_{3/2}$) photoelectron band. Experimental vertical ionization energies (I_v in eV) were calibrated by simultaneous addition of a small amount of argon to the sample.

$$PCl_3\,(g) + 3AgN_3\,(s) \longrightarrow P(N_3)_3\,(g) + 3AgCl\,(s) \quad (1)$$

$$AsCl_3\,(g) + 3AgN_3\,(s) \longrightarrow As\,(N_3)_3\,(g) + 3AgCl\,(s) \quad (2)$$

Geometric optimizations of all possible conformers for phosphorus triazide were performed using density functional theory methods, and three stable conformers for each triazide were located. The calculations were carried out at the B3LYP level of theory with a 6-311++G(3df) basis set. The B3LYP is a hybrid functional method based on Becke's three-parameter nonlocal exchange functional,[26] with Lee et al.'s nonlocal correlation.[27] For the arsenic triazide, geometry optimization was carried out according to the reported stable conformers[11] at the same level of theory. To assign the PES bands of both triazides, OVGF calculations were performed for those three stable conformers of $P(N_3)_3$ and $As(N_3)_3$ using the 6-311G(d) basis set based on optimized structures. The vertical ionization energy (E_v) was calculated at the ab initio level according to Cederbaum's outer valence Green's function (OVGF) method,[28] which includes the effect of electron correlation and reorganization beyond the Hartree–Fock approximation. The self-energy part was expanded up to the third order, and contributions of higher orders were estimated by means of a renormalization procedure. All calculations were performed using the Gaussian 98 program.[29]

Acknowledgments

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