

Dedicated to the memory of Prof. dr. Ioan Silaghi-Dumitrescu marking 60 years from his birth

A THEORETICAL APPROACH ON THE STRUCTURE OF ARSAALLENES -As=C=C< AND ARSAPHOSPHAALLENES -As=C=P-

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ABSTRACT. Calculations at the B3LYP/6-311 level were performed on a series of arsaallenes and arsaphosphaallenes of the type $RA_s=C=CR_2$ and $RA_s=C=PR$ in order to evaluate the nature of the As=C bond. The influence of several substituents (F, Cl, OMe, SiMe₃) on the order of the bond was also investigated.

Keywords: arsaallenes, arsaphosphaallenes, DFT calculations

INTRODUCTION

Derivatives of the type $E=C=E'$ ($E, E' =$ group 14 and 15 elements) have become the focus of research only in the last decades [1]. So far, only a few heteroallenic derivatives of the type $-As=C=E$ ($E = CR_2$ [2], PR [3], AsR [4]) have been isolated and structurally investigated. The arsenic – carbon distance has a small value of 1.758 Å as reported in $Mes^*As=C=AsMes^*$ ($Mes^* = 2,4,6$ -tri-*tert* butylphenyl) [4] and $Mes^*As=C=CR_2$ ($CR_2 =$ fluorenyl) [2]. The As-C-C bond angle for this derivative is 169.7°, with the central carbon atom deviated from the expected linearity. The supermesityl group lies at a 102° angle from the As=C double bond. For the arsaphosphaallene $Mes^*As=C=PMes^*$, problems of symmetry in the X-ray diffraction did not allow to determine exactly the bond lengths and bond angles [3].

We have previously investigated the nature of the As-C bond in heteroallenic derivatives of the type $As(V)=C=E$ ($As(V) = \lambda^5\sigma^4 As$), where $E=C, P(III)$ ($P(III) = \lambda^3\sigma^2 P$), [5]. A model for the structure of $H_3As=C=CH_2$ according to NBO analysis at the B3LYP/6-311G(d, p) level was proposed, in which As has a lone pair in an *sp* type orbital.

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A comparison with the analogues in which As has the formal oxidation state III can be very interesting, especially since there are more As(III) ($\text{As(III)} = \lambda^3\sigma^2 \text{As}$), derivatives of this type reported in the literature and the experimental data for doubly bonded As(V) is very scarce.

In order to assess the nature of the As-C bond in arsaallenes -As=C=C< and arsaphosphaallenes -As=C=P-, a theoretical investigation was carried out at the B3LYP/6-311G(d, p) level of the theory. Model compounds of the type RAs=C=CR₂ (R= H, Me, Ph), were studied as well as those in which one or two R groups have been replaced by one or two R' groups (R'= F, Cl, OMe, SiMe₃) on the As or the C atom. The same R' substituents were used for the arsaphosphaallenes. All geometries were optimized and a frequency calculation was run in order to verify if the obtained structures are indeed global minima. An NBO analysis was performed, in order to evaluate the nature of the orbitals involved in bonding and the Wiberg bond order for the As=C and C=C bonds was calculated for each case.

RESULTS AND DISCUSSION

For the model compound HAs=C=CH₂, the As=C bond has a length of 1.77 Å, in agreement with the experimental data obtained for the arsaallene Mes*As=C=CR₂ (1.758 Å) [2], and a bond order of 1.85. (The calculated bond order in the case of H₃As=C=CH₂ at the same level of theory was found to be 1.07). The calculated C=C bond length is 1.30 Å (1.314 Å by X-ray [2]). The geometry around the arsenic in HAs=C=CH₂ is angular, with the H-As-C bond angle of 94°. This suggests that the bonding involves the valence $4s^24p^3$ arsenic orbitals rather than hybrid ones, as expected for heavier main group elements. An NBO analysis shows that the lone pair on the As atom lies in an orbital with strong s character, and that almost pure p orbitals are contributing to the formation of the σ and π bonding to the carbon atom. The same is expected for the other arsaallenes investigated.

As for the only arsaallene characterized experimentally, Mes*As=C=CR₂, (As-C-C bond angle of 169.7°) the value of the angle As-C-C for HAs=C=CH₂ is not 180° but 173.8°. We can thus conclude that the deviation from the linearity of the allenic unit is not the result of steric hindrance or crystal-packing effects, but is inherent to the nature of the arsaallene. Moreover, the most significant second order interaction involves the As(III) lone pair as a donor and the antibonding s orbital of the C-C bond, which is also present for all the derivatives discussed below (figure 1). This interaction could account for the slight narrowing of the angle.

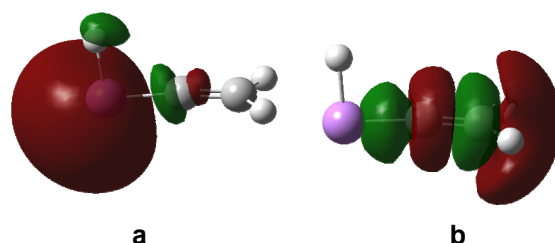


Figure 1. NB orbitals involved in second order perturbation interactions for $\text{HAs}=\text{C}=\text{CH}_2$. (a) lone pair electrons on As; (b) anti-bonding non-Lewis orbital on the C-C bond

I. Monosubstituted arsaallenes $\text{R}'\text{As}=\text{C}=\text{CR}_2$ and $\text{RAs}=\text{C}=\text{CRR}'$

In the case of substitution with one R' group ($\text{R}' = \text{F}, \text{Cl}, \text{OMe}$ and SiMe_3), two types of derivatives were considered: with R' on the arsenic, and on the terminal carbon atom of the allenic unit. The group R was either H , Me or Ph . The results obtained from the geometry optimization and NBO analysis are given in table 1.

It can be noticed that in every case the isomer bearing the R' group on the arsenic atom is more stable. However, in the case of substitution with SiMe_3 , the energy difference is significantly smaller. As in the case of As(V) derivatives, substitution of arsenic with an electron-withdrawing group or atom leads to a decrease in the bond order of the $\text{As}=\text{C}$ bond.

For the $\text{H}_2\text{AsC}_2\text{R}'$ isomers, there is a decrease of the bond order when going from $\text{HAs}=\text{C}=\text{CR}'\text{H}$ to $\text{R}'\text{As}=\text{C}=\text{CH}_2$, for $\text{R}' = \text{F}, \text{Cl}$, and OMe . This is explained by charge donation from the lone pairs of the R' to a vacant antibonding orbital of π symmetry on the $\text{As}-\text{C}$ bond. The value of the second order perturbation energy is 7.31 for $\text{R}' = \text{F}$, 5.15 for Cl and 11.30 for $\text{R}' = \text{OMe}$, which also reflects the magnitude of the bond order decrease. The two natural bonding orbitals involved in the interaction are illustrated in figure 2 for the case $\text{R}' = \text{OMe}$.

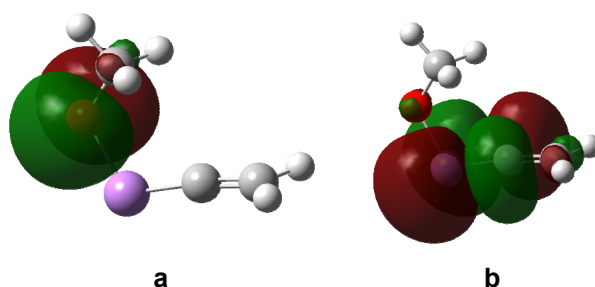


Figure 2. NB orbitals involved in second order perturbation interactions for $(\text{MeO})\text{As}=\text{C}=\text{CH}_2$. (a) lone pair electrons on O; (b) anti-bonding non-Lewis orbital on the C-C bond

However, for $R' = \text{SiMe}_3$, the bond order of the arsenic-carbon bond is higher in the case of $\text{Me}_3\text{SiAs}=\text{C}=\text{CH}_2$ (1.86, close to the bond order calculated for $\text{HAs}=\text{C}=\text{CH}_2$) than for the corresponding isomer, substituted at the terminal carbon atom, $\text{HAs}=\text{C}=\text{CH}(\text{SiMe}_3)$ (1.80). This is because in the case of the latter, there is a charge transfer from an orbital localized on $\text{C}_2\text{-Si}$ and the antibonding orbital of π symmetry of the As-C_1 bond. The two orbitals are shown in figure 3. The same phenomenon is observed for all SiMe_3 substituted derivatives.

Table 1. Selective data for $R'\text{As}=\text{C}=\text{CR}_2$ and $\text{RAs}=\text{C}=\text{CRR}'$, calculated at the B3LYP/6-311G(d, p) level (bond lengths in Å, bond angles in degrees). The Wiberg bond orders for $\text{As}=\text{C}$ and $\text{C}=\text{C}$ are also given.

Molecule	Energy (a.u.)	ΔE (kcal/mol)	As=C	C1=C2	As-C-C	W BO As=C	W BO C=C
$\text{HAs}=\text{C}=\text{CH}_2$	-2313.843087	-	1.77	1.30	173.8	1.85	2.02
$\text{MeAs}=\text{C}=\text{CMe}_2$	-2431.831534	-	1.76	1.31	173.5	1.84	1.88
$\text{PhAs}=\text{C}=\text{CPh}_2$	-3007.169658	-	1.76	1.32	172.7	1.81	1.80
$\text{HAs}=\text{C}=\text{CHF}$	-2413.096739	20.5	1.76	1.31	172.6	1.87	1.92
$\text{FAs}=\text{C}=\text{CH}_2$	-2413.129358	0.0	1.76	1.31	174.8	1.78	2.03
$\text{HAs}=\text{C}=\text{CHCl}$	-2773.461680	24.7	1.76	1.30	173.1	1.84	1.95
$\text{ClAs}=\text{C}=\text{CH}_2$	-2773.501019	0.0	1.76	1.31	174.1	1.81	2.01
$\text{HAs}=\text{C}=\text{CH}(\text{OMe})$	-2428.389328	11.8	1.76	1.31	170.5	1.88	1.87
$(\text{MeO})\text{As}=\text{C}=\text{CH}_2$	-2428.408053	0.0	1.76	1.31	172.6	1.74	2.03
$\text{HAs}=\text{C}=\text{CH}(\text{SiH}_3)$	-2722.591752	3.1	1.78	1.30	173.8	1.80	2.03
$(\text{Me}_3\text{Si})\text{As}=\text{C}=\text{CH}_2$	-2722.596750	0.0	1.76	1.31	176.1	1.86	1.98
$\text{MeAs}=\text{C}=\text{CMeF}$	-2491.763808	17.8	1.75	1.31	172.4	1.83	1.86
$\text{FAs}=\text{C}=\text{CMe}_2$	-2491.792168	0.0	1.75	1.32	175.4	1.81	1.87
$\text{MeAs}=\text{C}=\text{CMeCl}$	-2852.125134	24.3	1.76	1.30	173.2	1.80	1.90
$\text{ClAs}=\text{C}=\text{CMe}_2$	-2852.163852	0.0	1.75	1.31	175.1	1.84	1.85
$\text{MeAs}=\text{C}=\text{CMe}(\text{OMe})$	-2507.048261	13.2	1.75	1.32	175.1	1.86	1.82
$\text{MeOAs}=\text{C}=\text{CMe}_2$	-2507.069265	0.0	1.76	1.32	171.9	1.77	1.87
$\text{MeAs}=\text{C}=\text{CMe}(\text{SiMe}_3)$	-2801.246316	4.9	1.77	1.31	174.1	1.79	1.96
$(\text{Me}_3\text{Si})\text{As}=\text{C}=\text{CMe}_2$	-2801.254090	0.0	1.77	1.31	174.9	1.86	1.85
$\text{PhAs}=\text{C}=\text{CPhF}$	-2875.324550	17.4	1.75	1.32	170.4	1.79	1.80
$\text{FAs}=\text{C}=\text{CPh}_2$	-2875.352230	0.0	1.75	1.33	175.5	1.82	1.78
$\text{PhAs}=\text{C}=\text{CPhCl}$	-3235.682429	25.9	1.76	1.31	171.8	1.75	1.85
$\text{ClAs}=\text{C}=\text{CPh}_2$	-3235.723670	0.0	1.74	1.33	176.0	1.86	1.76
$\text{PhAs}=\text{C}=\text{CPh}(\text{OMe})$	-2890.618419	4.3	1.75	1.33	170.1	1.81	1.73
$\text{MeOAs}=\text{C}=\text{CPh}_2$	-2890.625224	0.0	1.75	1.32	174.0	1.81	1.79
$\text{PhAs}=\text{C}=\text{CPh}(\text{SiMe}_3)$	-3184.803748	6.8	1.77	1.31	174.8	1.75	1.92
$\text{Ph}(\text{SiMe}_3)\text{As}=\text{C}=\text{CPh}_2$	-3184.814571	0.0	1.76	1.32	174.2	1.89	1.76

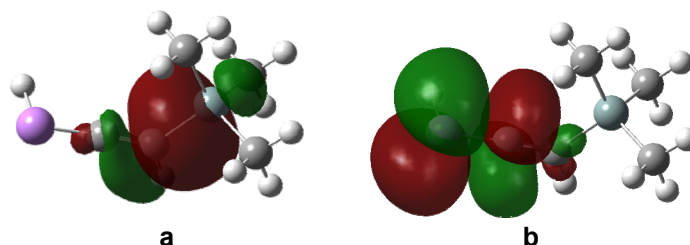


Figure 3. NB orbitals involved in second order perturbation interactions for $\text{HAs}=\text{C}=\text{CH}(\text{SiMe}_3)$. (a) σ orbital on the $\text{C}_2\text{-Si}$ bond; (b) π anti-bonding non-Lewis orbital on the $\text{As}=\text{C}_1$ bond

Going from the hydrogen to the methyl-substituted series, it can be noticed that the bond order for the fluorinated derivative decreases. The NBO analysis shows second order interactions between the π orbital situated on the As-C bond and a $\text{C}_2\text{-C}_3$ (from methyl) antibonding orbital, which lowers the bond order. The chlorinated species also display different values when $\text{R} = \text{Me}$. Thus, $\text{MeAs}=\text{C}=\text{CMeCl}$ has a lower bond order for the As-C bond than $\text{ClAs}=\text{C}=\text{CMe}_2$, in contrast with the hydrogen-substituted analogues. When the chlorine is on the carbon atom, a charge transfer occurs from the π orbital situated on the As-C and a σ^* (C-Cl) orbital, which was not present for $\text{HAs}=\text{C}=\text{CHCl}$. Also, the donation from the lone pairs of the Cl to the vacant antibonding orbital of π symmetry on the As-C bond is not present for the isomer $\text{ClAs}=\text{C}=\text{CMe}_2$, contrary to the case when $\text{R} = \text{H}$. The OMe and SiMe_3 -substituted derivatives behave like their analogues with hydrogen instead of methyl.

The only other notable exception is for the isomers $\text{PhAs}=\text{C}=\text{CPhF}$ (with a bond order of the As=C bond of 1.79) and $\text{FAs}=\text{C}=\text{CPh}_2$ (1.82). In this case, an interaction of the kind described for $\text{ClAs}=\text{C}=\text{CMe}_2$ influences the difference between the two values.

II. Disubstituted arsaallenes $\text{R}'\text{As}=\text{C}=\text{CRR}'$ and $\text{RAs}=\text{C}=\text{CR}'_2$

The same groups were considered in the case of the disubstitution by two R' groups. From the calculated energies presented in table 2, there can be noticed that the $\text{RAs}=\text{C}=\text{CR}'_2$ isomer is always energetically favored, but that in the case of $\text{R}' = \text{OMe}$ and SiMe_3 , the difference between the two types of derivatives is smaller. The bond order of the As=C bond is generally higher for $\text{R}'\text{As}=\text{C}=\text{CRR}'$ compounds, except when $\text{R} = \text{H}$, Me and $\text{R}' = \text{F}$, OMe and $\text{R} = \text{H}$, $\text{R}' = \text{Cl}$. This is due to donations from the lone pairs of F, Cl and O respectively to bonding orbitals on the As=C bond (mainly the one of π symmetry), similar to those described for $\text{R}'\text{As}=\text{C}=\text{CR}'_2$ (see figure 2 for the shape of the orbitals involved). The same considerations as before can be applied to explain the variation of the As=C bond order for the derivatives

with $R' = F, Cl$ and OMe . The silyl group is a special case, mainly because of the lack of lone pairs on the silicon, so it will be discussed in detail. From table 2, it can be seen that the $As=C$ bond order in is always smaller than in the corresponding isomer $Me_3SiAs=C=C(SiMe_3)R$. The explanation is similar as for the monosubstituted derivative, with a charge transfer from the bonding C_2-Si orbital (figure 4a, for $R = Me$) to both the σ (figure 4b) and the π anti-bonding orbitals localized on the $As-C$ bond. Only two such interactions are possible for $(Me_3Si)As=C=CR(SiMe_3)$, as opposed to four in the case of $RA_s=C=C(SiMe_3)_2$ derivatives (from both $C-Si$ bonding orbitals), which thus display a lower bond order.

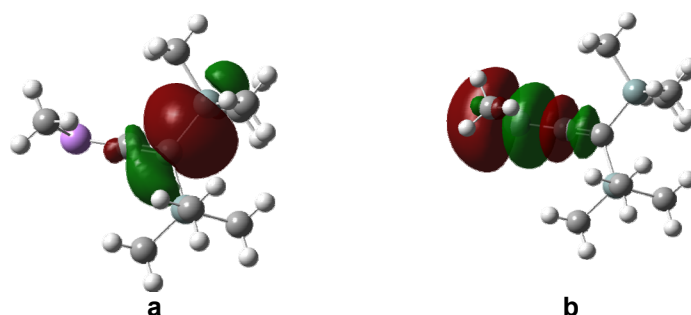


Figure 4. NB orbitals involved in second order perturbation interactions for $MeAs=C=C(SiMe_3)_2$. (a) σ -orbital on the C_2-Si bond; (b) σ -anti-bonding non-Lewis orbital on the $As=C_1$ bond

This bond order is even lower for $PhAs=C=C(SiMe_3)_2$. The NBO analysis shows that in this case, a supplementary charge transfer occurs from the p-symmetry bonding orbital on the $As-C$ bond to an antibonding orbital situated on a bond of the phenyl ring (see figure 5). This leads to a bond order of 1.67, the lowest for the entire series analyzed. However, $As-C$ distance is not greatly influenced.

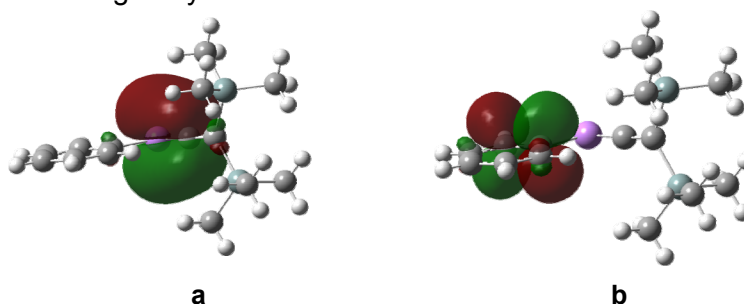


Figure 5. NB orbitals involved in second order perturbation interactions for $PhAs=C=C(SiMe_3)_2$. (a) π -orbital on the C_2-Si bond; (b) π -anti-bonding non-Lewis orbital on a $C=C$ bond of the phenyl ring

Table 2. Selective data for R'As=C=CRR' and RAs=C=CR'₂, calculated at the B3LYP/6-311G(d, p) level (bond lengths in Å, bond angles in degrees).
The Wiberg bond orders for As=C and C=C are also given.

Molecule	Energy (a.u.)	ΔE (kcal/mol)	As=C	C1=C2	As-C-C	W BO As=C	W BO C=C
FAs=C=CHF	-2512.387693	0.0	1.74	1.31	173.6	1.79	1.91
HAs=C=CF ₂	-2512.360844	16.8	1.75	1.30	170.9	1.86	1.84
ClAs=C=CHCl	-3233.120327	0.0	1.75	1.30	173.3	1.79	1.93
HAs=C=CCl ₂	-3233.075782	28.0	1.76	1.30	172.6	1.81	1.87
(MeO)As=C=CH(OMe)	-2542.956023	0.0	1.74	1.32	171.4	1.81	1.85
HAs=C=C(OMe) ₂	-2542.948974	4.4	1.75	1.33	162.8	1.88	1.73
(SiMe ₃)As=C=CH(SiMe ₃)	-3131.345021	0.0	1.77	1.31	175.1	1.80	1.98
HAs=C=C(SiMe ₃) ₂	-3131.339292	3.6	1.79	1.30	174.3	1.72	2.05
FAs=C=CMeF	-2551.724813	0.0	1.74	1.31	174.5	1.80	1.84
MeAs=C=CF ₂	-2551.693708	19.5	1.75	1.30	171.0	1.81	1.85
ClAs=C=CMeCl	-3272.454314	0.0	1.75	1.31	174.0	1.79	1.86
MeAs=C=CCl ₂	-3272.408031	29.0	1.75	1.30	172.9	1.77	1.89
(MeO)As=C=CMe(OMe)	-2582.284328	0.0	1.74	1.32	170.0	1.82	1.79
MeAs=C=C(OMe) ₂	-2582.274268	6.3	1.75	1.32	171.9	1.84	1.81
(SiMe ₃)As=C=CMe(SiMe ₃)	-3170.670114	0.0	1.77	1.31	175.1	1.80	1.93
MeAs=C=C(SiMe ₃) ₂	-3170.666509	2.3	1.78	1.30	174.6	1.72	2.03
FAs=C=CPhF	-2743.507094	0.0	1.74	1.32	171.9	1.81	1.77
PhAs=C=CF ₂	-2743.472533	21.7	1.75	1.30	168.9	1.76	1.85
ClAs=C=CPhCl	-3464.233759	0.0	1.74	1.31	173.6	1.80	1.80
PhAs=C=CCl ₂	-3464.186502	29.7	1.76	1.30	172.5	1.71	1.90
(MeO)As=C=CPh(OMe)	-2774.066178	0.0	1.74	1.32	169.6	1.81	1.79
PhAs=C=C(OMe) ₂	-2774.05281	8.4	1.75	1.32	170.8	1.80	1.81
(SiMe ₃)As=C=CPh(SiMe ₃)	-3362.450222	0.0	1.77	1.31	175.2	1.82	1.87
PhAs=C=C(SiMe ₃) ₂	-3362.444627	3.5	1.78	1.30	174.6	1.67	2.05

III. Arsaphosphaallenes R'As=C=PR and RAs=C=PR'

In the case of arsaphosphaallenes, the bond order of the As=C bond is lower than that of the corresponding arsaallenes (e.g., 1.82 for HAs=C=PH and 1.84 for HAs=C=CH₂; for complete data see table 3). This is readily explained by the NBO analysis: there is electron donation from the lone pair of the phosphorus atom in the σ-symmetry antibonding orbital localized on the As-C bond. The orbitals involved are shown in figure 6 for MeAs=C=PMe. In addition, charge transfer from the As lone pair to vacant orbitals on the P-C is present, similarly to the case of arsaallenes. The bond order of the P-C bond varies from 1.80 to 1.98.

The calculated energies for the model compounds show that for R' = Cl, SiMe₃, the RAs=C=PR' isomer is energetically favored, while in the case of F and OMe, R'As=C=PR have lower energies. In both cases though, the

difference in energy is not significant, going up to only 7.1 kcal for $R' = \text{Cl}$ and $R = \text{Ph}$. This relatively low value comparatively to that calculated for arsaallenes can be accounted by close values of bond energies of R-P and R-As, which are significantly different for R-As and C-R [6].

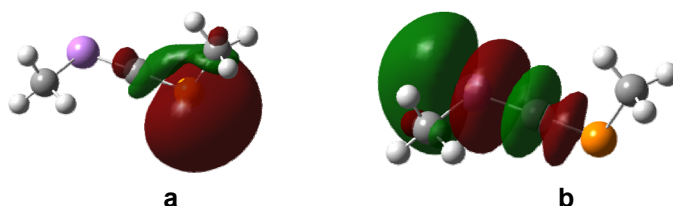


Figure 6. NB orbitals involved in second order perturbation interactions for $\text{MeAs}=\text{C}=\text{PMe}$. (a) lone pair on the P atom; (b) σ -anti-bonding non-Lewis orbital on the C=P bond

The value of the Wiberg bond order for the $\text{As}=\text{C}$ is always much lower for the $\text{RAs}=\text{C}=\text{P}(\text{SiMe}_3)$ derivatives than for $(\text{Me}_3\text{Si})\text{As}=\text{C}=\text{PR}$. This is explained by the NBO analysis in terms of a charge transfer from a P-Si bonding orbital to an antibonding orbital localized on the $\text{As}=\text{C}$ bond (see figure 7 for the shape of the NB orbitals involved). The values of the second order interactions are 18.70 for $R = \text{H}$, 15.96 for $R = \text{Me}$ and 14.72 for $R = \text{Ph}$. On the contrary, when Me_3Si group is on the arsenic atom, then the electron donation occurs from an As-Si orbital to an antibonding C-P orbital, which reduces the bond order of this bond for the $(\text{Me}_3\text{Si})\text{As}=\text{C}=\text{PR}$ compared to their isomers. The lack of this interaction explains the higher bond orders for $(\text{Me}_3\text{Si})\text{As}=\text{C}=\text{PR}$: 1.98 for $R=\text{H}$, 1.96 for $R=\text{Me}$ and 1.97 for $R=\text{Ph}$.

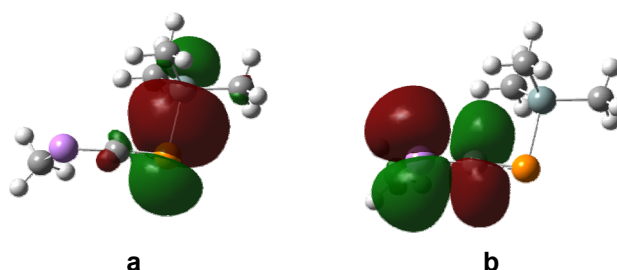


Figure 7. NB orbitals involved in second order perturbation interactions for $\text{MeAs}=\text{C}=\text{PSiMe}_3$. (a) σ -bonding orbital on the P-Si bond; (b) π -anti-bonding non-Lewis orbital on the As=C bond

As in the case of the arsaallenes, when $R = H$, $R' = F, Cl, OMe$, the lone pairs of the R' group play an important role in the value of the bond order of the $As=C$ bond. Thus, when the groups are bonded to arsenic, the donation of electrons from lone pairs to an antibonding orbital of p symmetry on the $As-C$ bond is present. For the $HAs=C=PR'$ isomers, this charge transfer occurs to the more available $P=C$ antibonding orbitals, leading to a decrease of the $P=C$ bond order when compared to its isomer or the simplest model compound, $HAs=C=PH$.

Table 3. Selective data for $RAs=C=PR'$ and $R'As=C=PR$, calculated at the B3LYP/6-311G(d, p) level (bond lengths in Å, bond angles in degrees). The Wiberg bond orders for $As=C$ and $C=C$ are also given.

Molecule	Energy (a.u.)	ΔE (kcal/mol)	As=C	C=P	As-C-P	W BO As=C	W BO C=P
$HAs=C=PH$	-2616.496293	-	1.77	1.64	170.1	1.82	1.94
$MeAs=C=PMe$	-2695.159405	-	1.76	1.64	170.5	1.79	1.89
$PhAs=C=PPh$	-3078.717049	-	1.76	1.64	168.6	1.74	1.84
$HAs=C=PF$	-2715.785965	0.0	1.76	1.64	168.0	1.83	1.83
$FAs=C=PH$	-2715.782567	2.1	1.76	1.64	170.2	1.73	1.94
$HAs=C=PCl$	-3076.145363	5.5	1.77	1.63	168.6	1.79	1.89
$ClAs=C=PH$	-3076.154206	0.0	1.76	1.64	169.6	1.76	1.92
$HAs=C=P(OMe)$	-2731.064527	0.0	1.76	1.64	166.8	1.84	1.81
$(MeO)As=C=PH$	-2731.058053	4.1	1.76	1.64	167.8	1.72	1.95
$HAs=C=P(SiMe_3)$	-3025.251322	1.1	1.78	1.63	172.2	1.72	1.98
$(Me_3Si)As=C=PH$	-3025.253113	0.0	1.76	1.65	171.7	1.85	1.86
$MeAs=C=PF$	-2755.119568	0.0	1.76	1.63	168.1	1.77	1.84
$FAs=C=PMe$	-2755.117374	1.4	1.76	1.64	170.3	1.74	1.88
$MeAs=C=PCl$	-3115.478872	6.2	1.76	1.63	169.0	1.74	1.89
$ClAs=C=PMe$	-3115.488827	0.0	1.76	1.64	169.7	1.78	1.86
$MeAs=C=P(OMe)$	-2770.397116	0.0	1.76	1.64	167.9	1.80	1.81
$MeOAs=C=PMe$	-2770.392069	3.2	1.76	1.64	168.4	1.73	1.89
$MeAs=C=P(SiMe_3)$	-3064.580612	2.0	1.78	1.64	172.3	1.71	1.96
$(Me_3Si)As=C=PMe$	-3064.583753	0.0	1.76	1.65	171.8	1.83	1.84
$PhAs=C=PF$	-2946.898555	0.0	1.76	1.63	156.3	1.71	1.85
$FAs=C=PPh$	-2946.897732	0.5	1.76	1.64	167.7	1.75	1.81
$PhAs=C=PCl$	-3307.257729	7.1	1.77	1.63	168.0	1.68	1.91
$ClAs=C=PPh$	-3307.269059	0.0	1.75	1.64	168.6	1.79	1.79
$PhAs=C=P(OMe)$	-2962.176075	0.0	1.76	1.64	165.5	1.74	1.81
$MeOAs=C=PPh$	-2962.172192	2.4	1.76	1.64	166.4	1.73	1.83
$PhAs=C=P(SiMe_3)$	-3256.35854	3.0	1.78	1.64	171.8	1.67	1.97
$Ph(SiMe_3)As=C=PPh$	-3256.363293	0.0	1.76	1.65	171.1	1.84	1.79

For $\text{MeAs}=\text{C}=\text{PCl}$, electron donation from the $\text{As}=\text{C}$ bond to an orbital situated on the $\text{P}-\text{Cl}$ bond occurs, which lowers the bond order. This interaction is present for $\text{R} = \text{Ph}$, but not for $\text{R} = \text{H}$, which explains the difference in the values of the $\text{As}-\text{C}$ bond order when changing the R group.

CONCLUSIONS

The $\text{As}-\text{C}$ bond in arsa- and arsaphosphaallenes has a calculated bond order between 1.67 and 1.90. The bonding of the arsenic in such derivatives involves the 'pure' atomic shell orbitals $4s$ and $4p$, with the lone pair being situated in the s orbital. The strength of the bond is influenced by functionalization on both the arsenic and the terminal element of the $\text{As}=\text{C}=\text{E}$ ($\text{E} = \text{C}, \text{P}$) unit. Substituents bearing lone pairs can influence it significantly, by charge transfer from the lone pairs to anti-bonding orbitals of the bond. The calculations indicate that increase of the bond order is favored by the presence of silyl groups on the arsenic atom, which can also afford the steric protection needed.

Whatever the group on As , C and P , the $\text{As}=\text{C}$, $\text{C}=\text{C}$ and $\text{C}=\text{P}$ bond lengths are about the same within 2 or 3 pm.

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The computational resources acquired through the CMMCCC program (Capacitati, modul I, 130/14.09.2007) were employed.

COMPUTATIONAL DETAILS

The calculations were performed using the Gaussian 09 package [7], at the B3LYP [8]/6-311G (d, p) level of the theory. The results were visualized with GaussView 4.1. The input geometry was also built with GaussView; in every case the starting geometry included the $\text{As}=\text{C}$ double bond. The structures were optimized and a vibrational analysis was performed in every case. Negative frequencies higher than -20 cm^{-1} were ignored. An NBO analysis was requested, together with a calculation of the Wiberg bond order, which was listed for the $\text{As}=\text{C}$ and $\text{C}=\text{C}/\text{P}$ bonds.

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