

An *ab initio* study of diarsacyclobutadienes

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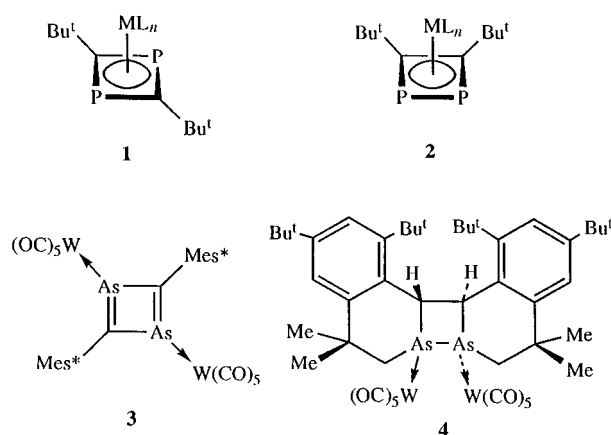
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Møller-Plesset MP2/6-311G* and MP4SDQ/6-311G* calculations have been made for the various possible ground state conformers of the simple 1,2- and 1,3-diarsacyclobutadienes (AsCH)₂, in order to determine their geometries, the nature of the bonding, and the relative stabilities of different isomers. These calculations revealed some qualitative differences between the analogous 1,2- and 1,3-diphosphacyclobutadienes. The most stable (gas phase) isomeric form of (AsCH)₂ is predicted to be 1,2-diarsatetrahedrane. Additionally, the mono- and di-substituted compounds Bu^t(AsC)₂H, Bu^t(AsC)₂Bu^t, Ph(AsC)₂H and Ph(AsC)₂Ph have been optimized. These indicate that 1,3-diarsacyclobutadienes prefer a planar C_{2h}-like ring structure with localized single and double As–C bonds.

Introduction

The last 15 years have seen phosphalkynes (P≡CR) transformed from chemical curiosities to versatile synthetic building blocks. Perhaps the most exciting property of these species is their ability to undergo thermal or metal-catalysed cyclo-oligomerization reactions.¹ Most commonly, phosphalkynes have been shown to undergo head-to-tail or head-to-head dimerizations at transition metal centres to form 1,3- and 1,2-diphosphacyclobutadiene complexes (**1** and **2**, respectively).² In all such complexes the heterocyclic ligand is either fully or partially delocalized and η⁴ co-ordinated to the metal fragment. Interestingly, there have been no reports of λ³,λ³-diphosphacyclobutadienes in the free state or solely η¹ co-ordinated through the phosphorus lone pair, though the free heterocycles have been implicated as intermediates in the formation of several P-substituted organic cage compounds.¹ Although not yet experimentally observed, unco-ordinated diphosphacyclobutadienes have been the subject of a number of theoretical studies³ which concluded that they are generally more stable than monomeric phosphalkynes.



Until recently, there had been no reports of analogous diarsacyclobutadienes or their transition metal complexes. This is mainly due to the absence of suitable (thermally stable) arsaalkynes with the potential to be dimerized. The one exception to this is As≡CMes* (Mes* = 2,4,6-C₆H₂Bu^t),⁴ and we have successfully treated this ligand with [W(CO)₅(thf)] to yield a 1,3-diarsacyclobutadiene complex **3** and a 1,2-diarsacyclobutadiene complex **4**.⁵ Surprisingly the As–C double bonds in **3** are completely localized and the heterocycle is only η¹-bonded to the W(CO)₅ moieties through the arsenic lone pairs. As already

mentioned, such structural characteristics are unknown in analogous 1,3-diphosphacyclobutadiene complexes. In addition, we believe **4** is formed *via* an intermediate 1,2-diarsacyclobutadiene complex which undergoes an intramolecular rearrangement.

In order to shed light on the structural differences between complex **3** and known diphosphacyclobutadiene complexes,⁶ we have undertaken *ab initio* calculations on the parent 1,2- and 1,3-diarsacyclobutadienes (AsCH)₂ and some of their valence isomers. In addition, the effect of one and two tertiary butyl or phenyl substituents has been explored. This appears to be the first *ab initio* study of diarsacyclobutadiene, its valence isomers and some substituted products.

Computational details

Initial Hartree–Fock (HF) geometry optimizations employed GAMESS⁷ running on DEC Alpha RISC workstations. All molecules were first optimized using HF/6-31G* basis sets,⁸ followed by HF and MP2-level optimizations with GAUSSIAN 94⁹ running on the ‘Columbus’ Computational Chemistry facility at Rutherford Appleton Laboratories with the larger 6-311G* basis sets on all atoms.¹⁰ (For some of the larger species, MP2-level optimizations were too computationally demanding.) Improved total energies were obtained for the (AsCH)₂ species from single-point MP4SDQ/6-311G* calculations at the MP2/6-311G* geometries. Harmonic frequency calculations HF/6-311G* and MP2/6-311G* were also performed for the same species in order to obtain thermal energies, and to establish whether a given conformer is at an energy minimum. Single point configuration interaction calculations including all single excitations (CIS) were made at the ground state-optimized geometries for the two most stable isomers of (AsCH)₂, to check for any low-lying singlet or triplet states.

Analyses of the charge distributions and bonding have been carried out at the MP2 level using both the Natural Population Analysis (NPA) developed by Foster and Weinhold,¹¹ and the Atoms-In-Molecules (AIMs) and topological techniques¹² and programs¹³ developed by Bader and co-workers.

More complete details of the structures, energies, frequencies and charge distribution/bonding analyses are available from the authors on request.

Results and discussion

(a) Structures and energetics

Fig. 1 illustrates the structures of the ten compounds optimized

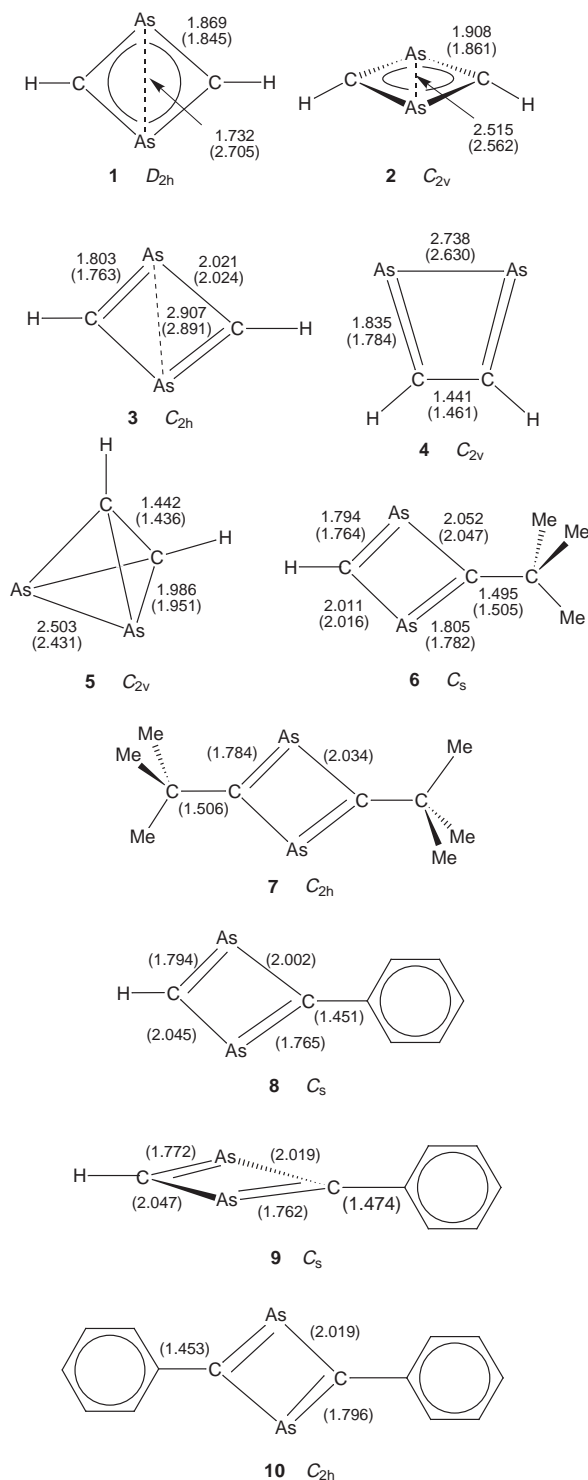


Fig. 1 The ten compounds optimized in this study, with MP2/6-311G* geometrical parameters in Å (Hartree-Fock values in parentheses).

in this work, which includes five isomers of $(\text{AsCH})_2$. Table 1 reports the associated electronic and thermal vibrational energies (at 298 K). Structures 1–5 are the conformers/isomers of $(\text{AsCH})_2$ in various possible symmetries. The most symmetric structure (1) is delocalized with four As–C bonds of equal length, intermediate between the typical single As–C bond (≈ 2.0 Å) and double bond (≈ 1.8 Å). However, a frequency calculation shows that this is a saddle-point conformer (see Table 1). Possible distortions of the ring from 1 include ‘folding’ it about the $\text{C}\cdots\text{C}$ axis, such that the arsenic atoms approach one another (possibly) forming an As–As bond, or allowing the equivalent As–C bonds to relax to form pairs of double and single bonds, retaining a planar form. [A conformer of 1,3-

Table 1 Electronic and thermal energies (at 298 K) for various conformers of $(\text{AsCH})_2$, in kJ mol^{-1}

Conformer/ isomer	ΔE			Thermal energy ^d	No. of imaginary frequencies
	MP4 ^a	MP2 ^b	HF ^c		
1	+72.4	+90.3	+22.8	72.4	2
2	+18.5	+12.6	–0.8	84.2	1
3	–39.7	–19.2	–47.8	83.5	0
4	–116.8	–103.4	–130.5	87.7	0
5	–137.4	–147.3	–152.5	82.7	0
2 AsCH	0.0	0.0	0.0	76.9	0

^a Electronic energy at the MP4SDQ/6-311G*//MP2/6-311G* level, relative to two AsCH molecules ($E = -2272.80010$ au for AsCH) at the same level; $\text{au} = E_{\text{h}} \approx 4.36 \times 10^{-18}$ J. ^b Electronic energy at the MP2/6-311G*//MP2/6-311G* level, relative to two AsCH molecules ($E = -2272.78989$ au for AsCH) at the same level. ^c Electronic energy at the HF/6-311G*//HF/6-311G* level, relative to two AsCH molecules ($E = -2272.53614$ au for AsCH) at the same level. ^d Unscaled thermal energies computed in the harmonic approximation at the MP2/6-311G*//MP2/6-311G* level.

diarsacyclobutadiene with even lower (C_2) symmetry, in which the ring is both folded and has localized single and double As–C bonds, could not be found.] These correspond to conformers 2 and 3, respectively. Frequency calculations show that 2, although significantly lower in energy than 1, is also at a transition state, while 3 is stable and is the lowest energy conformer of 1,3-diarsacyclobutadiene. This is in agreement with experiment, since this planar C_{2h} -like conformation is observed in the only known 1,3-diarsacyclobutadiene.⁵ At the MP4/6-311G* level it is predicted to be stable relative to two $\text{As}=\text{CH}$ molecules by 33.1 kJ mol^{-1} (including the change in thermal energy), *i.e.* it is a possible stable product of $\text{As}=\text{CH}$ dimerization, although the binding energy is not particularly large. This differs from the analogous 1,3-diphosphacyclobutadiene, which is *unstable* relative to two $\text{P}=\text{CH}$ molecules.³

Species 4 and 5 are 1,2 isomers with a localized As–As single bond. Frequency calculations indicate that both are stable (no imaginary frequencies) and much lower in energy than 1,3-diarsacyclobutadiene. The 1,2-diarsacyclobutadiene conformer 4 is somewhat anomalous, with an As–As bond length of ≈ 2.74 Å which is much longer than the experimentally determined value of ≈ 2.42 Å in a metal-functionalised 1,2-diarsacyclobutadiene.⁵ Interestingly, this resembles what was found in the analogous conformer of 1,2-diphosphacyclobutadiene.³ Those authors found two stable conformers with this (planar) symmetry, differing only in the length of the P–P bond, but were unable to locate any transition state between them. Despite similar searching, we cannot find an analogous conformer with a shorter As–As bond.

The CIS calculations on compound 3, the 1,3-diarsacyclobutadiene isomer, gave a vertical excitation energy to the lowest-lying singlet state of 1.71 eV, and 1.40 eV to the lowest triplet state ($\text{eV} \approx 1.60 \times 10^{-19}$ J). The analogous results for the 1,2-diarsacyclobutadiene isomer 5 were 3.63 (singlet) and 2.39 eV (triplet). So in both cases there are no low-lying (< 1.0 eV) states which could cast doubt on the use of the MP2 method for studying the ground state structures and properties.

Species 6–10 correspond to a study of substituent effects on the (experimentally observed) planar C_{2h} -like $(\text{AsC})_2$ unit, using realistic substituent groups such as tertiary butyl and phenyl. Two conformers of $\text{Ph}(\text{AsC})_2\text{H}$ have been considered, in which the phenyl ring is either perpendicular to or coplanar with the $(\text{AsC})_2\text{H}$ moiety, respectively. At the HF/6-311G* level the latter is lower in energy by 19.6 kJ mol^{-1} . This is opposite to the experimentally observed case where the (Bu^t-substituted) phenyl groups are approximately perpendicular to the $(\text{AsC})_2$ plane, presumably due to solid-state steric interactions. In 6 and

Table 2 Some charge distribution features (MP2/6-311G* level)

Conformer/isomer	NPA As charge	AIMs As charge	AIMs As dipole ^a	$\epsilon(\text{As-C})^b$	$\epsilon(\text{As-As})^c$
1	+1.05	+1.039	1.723	0.11	—
2	+0.79	+0.823	1.549	0.15	—
3	+0.79	+0.838	1.655	0.01, 0.28	—
4	+0.40	+0.415	1.284	0.06	0.25
5	+0.42	+0.456	1.298	0.34	0.26
AsCH	+0.49	+0.635	1.331	0.00	—

^a Atomic dipole moment in au. ^b Ellipticity for As–C bond (two values given where two unique bonds are present). ^c Ellipticity for As–As bond, where present [*i.e.* a (3, –1) critical point in ρ was located between the atoms].

9 the C_s and in **10** the C_{2h} symmetry allowed arbitrary (planar) arrangements of atoms in the (AsC)₂ unit (since these atoms were always in symmetry planes), and the ring structures are perturbed from exact C_{2h} symmetry by up to ≈ 0.03 Å relative to the ‘parent’ species **3**. Nevertheless it is clear that the (AsC)₂ unit retains its C_{2h} -like shape upon monosubstitution of hydrogen by Bu^t or Ph. The disubstituted species **8** and **10** were optimized with C_{2h} symmetry, which would nevertheless have allowed the ring bond lengths to equalize to form a D_{2h} -like structure as in **1**, but localized single and double As–C bonds are evidently preferred.

(b) Charge distributions/bonding

The molecular dipole moment is non-zero in the three isomers of (AsCH)₂ **2**, **4** and **5** which have C_{2v} symmetry, with MP2/6-311G* values of 0.96, 1.08 and 1.11 D ($D \approx 3.33 \times 10^{-30}$ Cm) respectively (*i.e.* minimal variation between them).

One point of interest in all these compounds is whether an As–As bond is present. According to Bader and Essén,¹⁴ the existence of a (3, –1) critical point (CP) between two atoms is one of the necessary criteria for recognizing a bond between them. The CP is located where $\nabla\rho = 0$ (ρ being the electron density), and is assigned (n, m) according to the number of unique eigenvalues of the Hessian of ρ at this point (n) and the sum of the signs of these eigenvalues (m). Hence a (3, –1) or ‘bond’ CP shows one (bond-directed) positive curvature and two orthogonal (perpendicular) negative curvatures, meaning that ρ at this point minimizes along the bond and is simultaneously maximized with respect to any perpendicular direction. Such (3, –1) CPs were successfully located between arsenic atoms in the MP2/6-311G* density distributions of the 1,2 isomers **4** and **5**, but the 1,3 isomers each contain a so-called ‘ring’ CP (one negative, two positive curvatures) where a bond CP might have been anticipated. However, we note that **2**, which has an As...As distance quite typical for an As–As single bond, even the existence of a (3, –1) CP would not have been sufficient to indicate an As–As bond according to Bader and Essén,¹⁴ who stipulate that the molecule should also be in a stable equilibrium geometry.

The ratio of the two curvatures (λ_1, λ_2) of ρ perpendicular to a bond gives information on the bond order or degree of π bonding.¹⁵ ‘Bond ellipticities’, defined as $\epsilon = (\lambda_2/\lambda_1) - 1$, are reported in Table 2 for the bonds As–C and As–As (where present). These values clearly show that the As–C bonds in the (unstable) conformers **1** and **2** of 1,3-diarsacyclobutadiene are partly conjugated (a pure single bond has $\epsilon \approx 0$), compared to the localized double and single bonds in the stable conformer **3**. Although this could also be inferred from the bond lengths, ϵ measures have the advantage of being based on the shape of the electron distribution (*i.e.* they *directly* reflect the bonding, rather than the bond length which does so only indirectly). Moreover, it has recently been shown that P–C bond ϵ values do not correlate simply with bond lengths.¹⁶ That this also applies to As–C bonds is evident from the ϵ values for conformer **4** of 1,2-diarsacyclobutadiene, since the formally double bonds have very low ϵ values. The formally single (and anomalously long)

As–As bond has a relatively high ϵ value, almost identical to the value in the 1,2-diarsatetrahydroane conformer **5**, despite the fact that this bond is more than 0.2 Å shorter than the As–As bond in **4**.

Atomic charges for arsenic have been determined within both the NPA and AIMs schemes (Table 2). The latter also permits computation of atomic moments higher than the zeroth order (charge). Consequently, Table 2 also reports the AIMs arsenic atomic dipole values in the (AsCH)₂ isomers, since this may be used to characterize the lone pair distribution of an atom.^{17,18} The NPA and AIMs atomic charges agree that the 1,2 isomers carry the smallest positive charge and dipole on arsenic. The lower dipole values (compared to 1,3-diarsacyclobutadiene) indicate less charge density in the arsenic lone pair (*i.e.* more 4s character). It should be noted, however, that this does not necessarily imply a lower basicity.^{18,19}

Fig. 2(a)–2(e) are $-\nabla^2\rho$ distributions for the isomers of (AsCH)₂, in planes which contain the two arsenic atom nuclei and at least one carbon atom nucleus. This scalar function of ρ serves to illustrate regions of charge concentration (solid contours) and depletion (negative contours);^{20,21} its topological properties are the basis of modern VSEPR theory.²² Each arsenic atom shows three concentric concentrations of positive contours close to the nucleus, corresponding to the closed $n = 1, 2$ and 3 quantum shells. A striking feature of these maps is the depletion of the outer ($n = 4$) bonding shell of electrons, consistent with the positive charges for arsenic under either the AIMs or NPA schemes. The lone pair of arsenic appears in Fig. 2(a) and 2(c) as a small, isolated region of charge concentration, and the appearance of this region, like the AIMs dipole values, gives an indication of the hybridization of arsenic. The apparent loss of charge concentration in the lone-pair region of the C_{2h} conformer of 1,3-diarsabutadiene [map 2(c)] compared to the D_{2h} conformer [map 2(a)] corresponds with the previously discussed reduction of the atomic dipole, suggestive of increased 4s character of the arsenic lone pair in **3** compared to that in **1**. Interestingly, in map 2(d) the lone pair concentration is absent, which again is consistent with its (even smaller) dipole. In maps 2(b) and 2(e) corresponding to non-planar isomers of (AsCH)₂ the lone pair does not lie in the map plane, so it is absent for a different reason.

The ‘anomalous’ conformer **4** of 1,2-diarsacyclobutadiene, with its long As–As bond, shows a small isolated concentration of charge density in the middle of the bond, a feature rarely seen in equilibrium structures. Disappointingly it does not correspond to a so-called non-nuclear attractor (a maximum of charge density in the bond) since only a (3, –1) CP could be located.

Table 3 reports the natural electron configuration of the atoms for compounds **1–6** at the MP2 level of theory. The values for arsenic suggest an increase in the 4s and 4p character along the conformer/isomer series **1–5**. This is mostly at the expense of the carbon 2p orbital (and the 2s, to a lesser extent). Since the analysis presented earlier indicated *less* p-type character of the arsenic lone pair hybrid in planar isomers **3** and **4** compared to **1**, it must be the bond-directed 4s4p hybrid orbitals which contain more charge in **3** and **4**.

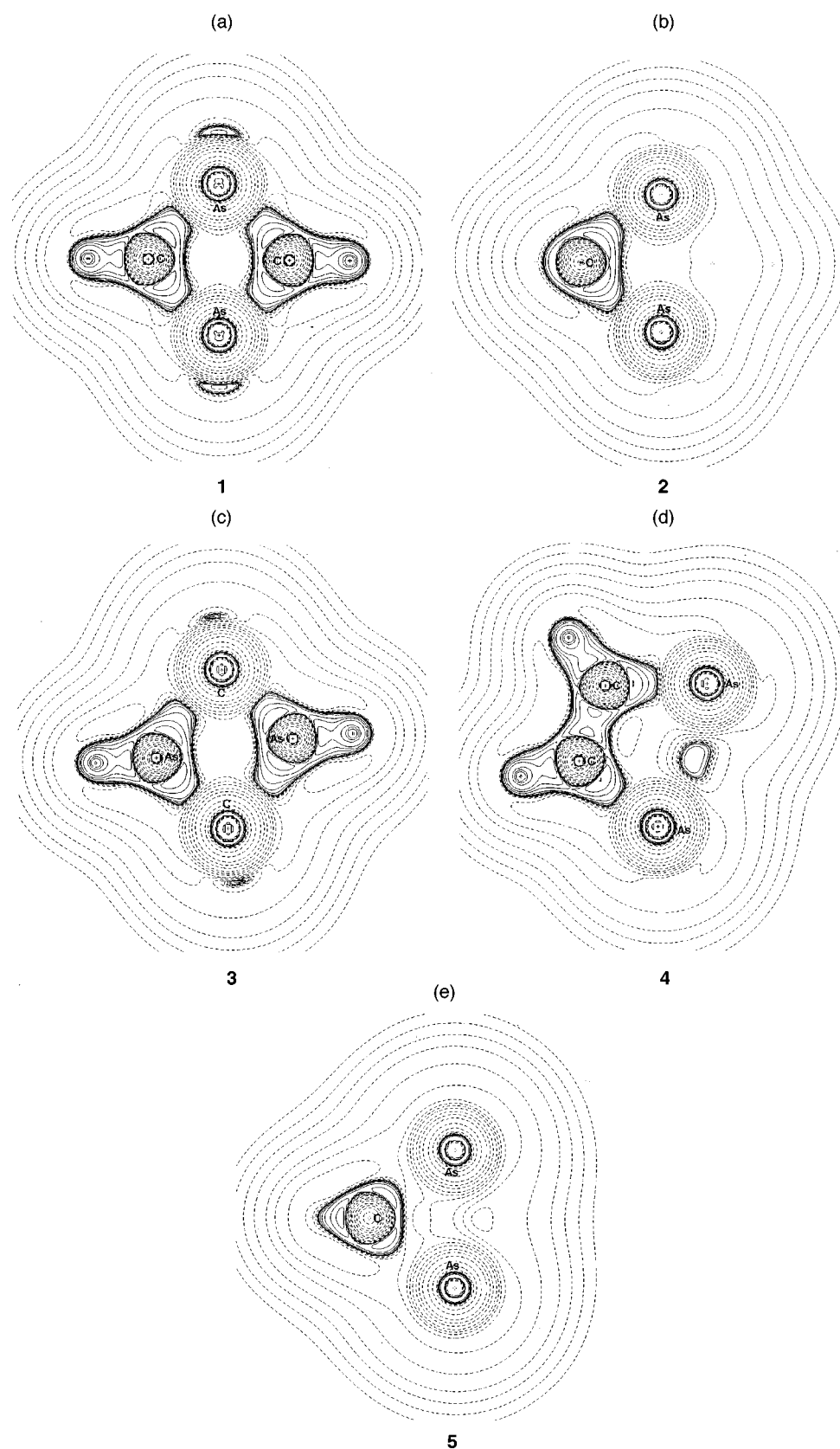


Fig. 2 The $-\nabla^2\rho$ distributions for conformers/isomers 1–5 of $(\text{AsCH})_2$. All maps are plotted in planes containing both arsenic atoms and at least one carbon.

Conclusion

Ground state 1,3-diarsacyclobutadiene exists in a stable planar (C_{2h}) conformation. It is stable relative to two AsCH molecules, but the relatively small binding energy of $\approx 30 \text{ kJ mol}^{-1}$ suggests that it would not be easy to stabilize this compound by dimer-

ization of $\text{As}=\text{CH}$ (except perhaps at low temperatures). Neither tertiary butyl nor phenyl substituents force the $(\text{AsC})_2$ sub-unit to adopt a planar D_{2h} -like structure with equivalent $\text{As}-\text{C}$ bonds. By far the most stable isomer of $(\text{AsCH})_2$ is the 1,2- 'cage' isomer 1,2-diarsatetrahydrene.

A combination of methods, including analysis of the total

Table 3 Natural electron configurations (MP2/6-311G* level)

Conformer/ isomer	Arsenic	Carbon	Hydrogen
1	[core]4s ^{1.60} 4p ^{2.27}	[core]2s ^{1.27} 2p ^{3.93}	1s ^{0.77}
2	[core]4s ^{1.64} 4p ^{2.49}	[core]2s ^{1.36} 2p ^{3.57}	1s ^{0.79}
3	[core]4s ^{1.64} 4p ^{2.50}	[core]2s ^{1.30} 2p ^{3.63}	1s ^{0.79}
4	[core]4s ^{1.75} 4p ^{2.77}	[core]2s ^{1.13} 2p ^{3.41}	1s ^{0.79}
5	[core]4s ^{1.77} 4p ^{2.74}	[core]2s ^{1.11} 2p ^{3.47}	1s ^{0.75}
AsCH	[core]4s ^{1.71} 4p ^{2.72}	[core]2s ^{1.28} 2p ^{3.38}	1s ^{0.79}
6	[core]4s ^{1.61} 4p ^{2.49}	[core]2s ^{1.29} 2p ^{3.67}	1s ^{0.79}

electron density and natural population analysis, showed how the distribution of the charge density around the arsenic atom in (AsCH)₂ evolves from the (unstable) forms **1** and **2** to the stable forms **3**, **4** and **5**. The former contain a more prominent arsenic lone pair, whilst in the latter charge has transferred from both the lone pair and the carbon atoms bonded to arsenic into the 4s4p bond-directed hybrids.

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