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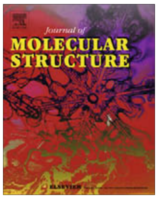

Equilibrium CAs and CSb bond lengths

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ABSTRACT

The equilibrium structures of some small molecules containing the CAs or the CSb bond are determined using the method of predicate observations. The input data are the semi-experimental equilibrium rotational constants (experimental ground state rotational constants corrected for the rovibrational contribution calculated from the *ab initio* cubic force field) and the bond lengths and bond angles calculated *ab initio* using the CCSD(T) method and a relativistic effective core potential of quadruple zeta quality. It is shown that this method, avoiding difficult isotopic substitutions, allows us to obtain reliable equilibrium structures.

1. Introduction

The equilibrium CX bond lengths are accurately known for different atoms X in many molecules where X = H [1], C [2], N [3], O [3], F [4], and Hal (where Hal = Cl, Br, and I) [5]. On the other hand, data for the CAs and CSb bond lengths are extremely scarse. For the CAs bond, the microwave spectra of difluoromethylarsine, CH_3AsF_2 [6], ethylidynearsine, CH_3CAs [7,8] and trimethylarsine, $(CH_3)_3As$ [9] have been measured and the structure of arsabenzene, *c*-C_5H_5As, has been investigated by microwave spectroscopy [10] and by electron diffraction [11]. For all these molecules, an approximate value of the CAs bond length has been estimated, but, with the exception of CH_3CAs [8], this estimation was based on many assumptions and it is thus rather inaccurate, see Table 1. For the CSb bond length, the data are still more scarse, only the microwave spectra of vinylstibine, $H_2C{=}CHSbH_2$ [12], and stibabenzene, *c*-C_5H_5Sb [13] have been measured leading to a very approximate value of the CSb bond length (see Table 1).

In addition to that, the microwave spectra of vinylarsine, $H_2C{=}CHAsH_2$ [14] ethynylarsine, $HC{\equiv}CAsH_2$, and ethylarsine, $CH_3CH_2AsH_2$ [15] have also been recently measured in our laboratories allowing us to obtain very accurate ground state rotational constants. The microwave spectrum of methylarsine, CH_3AsH_2, has also been measured but never published [16]. These experimental ground state rotational constants do not permit to calculate an equilibrium structure but they can be corrected using *ab initio* rotation–vibration interaction constants (α-constants) in order to obtain semi-experimental equilibrium rotational constants [17]. With the exception of CH_3CAs, the number of rotational constants is not large enough to determine an equilibrium structure. However, each molecule may be divided in three parts: (i) the alkyne (hydrocarbon) group, C_mH_n, whose structure may be accurately computed using standard *ab initio* methods; (ii) the arsine (resp. stibine) group, AsH_2 (resp. SbH_2) whose *ab initio* structure may be scaled using the known equilibrium structure of AsH_3 [18] (resp. SbH_3 [19]); (iii) the CX (X = As, Sb) bond length and the $\angle$(CCX) bond angle whose values may be crudely estimated using *ab initio* methods. The goal of this paper is to show that it is possible to obtain a reliable equilibrium structure for these molecules by combining the *ab initio* equilibrium structure and the semi-experimental rotational constants in the method of predicate observations. In this method, the rotational constants and the *ab initio* structure are used as input in a least-squares fit, each datum being weighted according to the value of its estimated uncertainty [20,21] .

The paper is organized as follows. Section 2 describes the *ab initio* calculations. Section 3 is dedicated to the equilibrium structure of CH_3CAs. Section 4 is devoted to the structure of $HC{\equiv}CAsH_2$. This section is more detailed than others because it explains the methodology used which is then applied in the subsequent sections to the other molecules, $CH_2{=}CHAsH_2$, $CH_3CH_2AsH_2$, and $CH_2{=}CHSbH_2$.

2. *Ab initio* calculations

Geometry optimizations have been carried out at two levels of electronic structure theory, second-order Møller–Plesset perturbation theory (MP2) [22] and coupled-cluster (CC) method with single and double excitations (CCSD) [23] augmented by a perturbational estimate of the effects of connected triple excitations [CCSD(T)] [24]. For the H and C atoms, Dunning's

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Table 1
Previous determinations of the CAs or the CSb bond length (values in Å).

Molecule	Bond	Structure[a]	value	Ref.
$(CH_3)_3As$	C–As	r_0	1.959(10)	[9]
CH_3AsF_2		r_0	1.92(10)	[6]
c-C_5H_5As		r_g	1.850(3)	[11]
CH_3CAs		r_e[b]	1.658(2)	[8]
c-C_5H_5Sb	C–Sb	r_0	2.050(5)	[13]
$CH_2{=}CHSbH_2$		r_s	2.13(3)	[12]

[a] r_0 = effective structure from ground state rotational constants, r_g = average internuclear distance at thermal equilibrium from electron diffraction, r_e = equilibrium structure, r_s = substitution structure.

[b] Extrapolated from the average structure (r_z).

correlation-consistent polarized valence n-uple zeta basis sets, cc-pVnZ [25] with n {T, Q} were employed. For the As and Sb atoms, the correlation-consistent valence basis sets with the Stuttgart-Dresden-Bonn relativistic effective core potential, SDB-cc-pVnZ [26] (abbreviated as SDB-VTZ) were used. In all calculations, the frozen core approximation was used, unless otherwise stated.

The anharmonic force field was calculated at the MP2 level of theory using the SDB-cc-pVTZ basis set. There is indeed a large documented evidence which shows that, in most cases, the CCSD(T) force field only provides a negligible improvement over the MP2 force field in determining the semi-experimental equilibrium structure [27,28]. This will be further checked here in the particular case of CH_3CAs. The reference geometry was first determined via optimization prior to computing the force field at the same level of theory. Then, the associated harmonic force field was evaluated analytically in Cartesian coordinates. The cubic (ϕ_{ijk}) and semidiagonal quartic (ϕ_{ijkk}) normal coordinates force constants were determined with the use of a finite difference procedure involving displacements [29] along reduced normal coordinates and the calculation of analytic second derivatives at these displaced geometries. This procedure was repeated for all isotopologues. The semi-experimental equilibrium rotational constants needed to determine a semi-experimental equilibrium structure are then obtained by correcting the experimental ground state rotational constants with the α-constants, computed from the *ab initio* cubic force field via the expression

$$B_e^\xi = B_0^\xi + \sum_i \alpha_i^\xi \frac{d_i}{2} \tag{1}$$

where $\xi = a, b, c$, referring to the principal axes of the molecule; the sum is running over all normal modes and d_i is a degeneracy factor (1 for non-degenerate vibrations and 2 for doubly-degenerate vibrations). The evaluation of the α-constants as well as the other spectroscopic parameters was based on second-order perturbation theory [30].

For the calculation of the magnetic g-tensor, the Kohn-Sham density functional theory [31] using Becke's three-parameter hybrid exchange functional [32] and the Lee-Yang-Parr correlation functional [33] together denoted as B3LYP, was also employed together with the split-valence basis set 6-311G(3df,2pd), as implemented in GAUSSIAN03 (g03) [34] for the H,C and As atoms. For molecules containing Sb, the DGDZVP basis set, as implemented in g03, was used. The diagonal elements of the g-tensor permit to calculate the electronic correction to the rotational constants using the relation

$$B_{\mathrm{corr}}^\xi = \frac{B_{\mathrm{exp}}^\xi}{1 + (m/M_p)g_{\xi\xi}} \tag{2}$$

where $g_{\xi\xi}$ is expressed in units of the nuclear magneton, m is the electron mass, and M_p the proton mass. The calculated values of the g-tensor are given in Table S1 of the Supplementary material. This correction was found negligible for all molecules of this work.

All computations were performed with g03.

3. Ethylidynearsine

Ethylidynearsine, CH_3CAs, is the most promising molecule from the point of view of structure determination because it has already been thoroughly studied. The ground state rotational constants of eight isotopologues have been determined, its infrared spectrum has been measured, an average structure (r_z) has been calculated and an approximate equilibrium structure has been deduced [8].

The anharmonic force field, calculated at the MP2/SDB-VTZ level of theory, was used to calculate the values of the spectroscopic parameters for which experimental values are known: quartic centrifugal distortion constants and band centers. The results are given in Table S2 of the Supplementary material. The good agreement between the calculated and experimental parameters indicates that the force field is reliable.

The semi-experimental (se) equilibrium structure was calculated from a weighted least-squares fit of the related equilibrium moments of inertia and is given in Table 2. The system of normal equations is moderately well conditioned (condition number $\kappa = 264$) [35]. This is mainly due to the fact that there is no isotopic substitution available for As. However, the standard deviation of the derived parameters is extremely small, indicating that the r_e(se) structure should be accurate. The semi-experimental structure is in very good agreement with the previous equilibrium structure (extrapolated from the r_z structure), but it is much more accurate. The *ab initio* structures are also given in Table 2. The CCSD(T)/SDB-VQZ values with all electrons correlated are in very good agreement with the semi-experimental structure. For the methyl part, it was expected [36] but for the CAs bond length, it might be accidental. The CC bond length, at 1.463 Å, is longer than in methyl cyanide (1.459 Å) [27] indicating a smaller degree of double bond character. Finally, it as to be noted that the CH bond length at 1.0910(3) Å is longer than in CH_3CN where the value is 1.0865(1) Å [27]. This is in agreement with the fact that the CH stretching frequencies are larger in CH_3CN than in CH_3CAs. For instance, the CH_3 symmetric stretch, ν_1, is at 2840 cm^{-1} in CH_3CAs [8] and 2954 cm^{-1} in CH_3CN [27].

4. Ethynylarsine, $HCCAsH_2$

The experimental ground state rotational constants of $HC{\equiv}CAsH_2$, $B_0 = 3666.1654(6)$ MHz and $C_0 = 3659.6748(6)$ MHz [15] are corrected with the α-constants from the MP2/SDB-VTZ force field to give the semi-experimental equilibrium rotational constants, $B_e = 3659.3(2)$ MHz and $C_e = 3652.8(2)$ MHz where the quoted uncertainty takes into account the uncertainty on the *ab initio* α-constants. The *ab initio* structure has been optimized at

Table 2
Structure of ethylidynearsine, CH_3CAs (distances in Å, angles in degrees).

Method	Basis set	r(CH)	r(CC)	r(CAs)	∠(HCC)
r_0[a]		1.105(7)	1.465(2)	1.660(1)	110.6(2)
r_e[b]		1.091(3)	1.465(2)	1.658(2)	110.6(2)
MP2 fc[c]	SDB-VTZ	1.090	1.466	1.677	110.71
CCSD(T) ae[c]	SDB-VQZ	1.090	1.465	1.659	110.71
r_e(se)[d]		1.0910(3)	1.4634(2)	1.6585(2)	110.575(10)

[a] r_0 = effective structure from a fit of the ground state rotational constants, Ref. [8].

[b] Extrapolated from the average structure (r_z), Ref. [8].

[c] fc = frozen core approximation, ae = all electrons correlated.

[d] Semi-experimental equilibrium structure.