

Available online at www.sciencedirect.com



Chemical Physics Letters 411 (2005) 14-17



www.elsevier.com/locate/cplett

# The relative stability of the two isomers of AlP<sub>3</sub>

Thaciana Malaspina, Kaline Coutinho, Sylvio Canuto \*

Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970 São Paulo, SP, Brazil

Received 10 January 2005; in final form 1 June 2005 Available online 22 June 2005

#### Abstract

The relative stability of the two lowest singlet states of AlP<sub>3</sub> ( $C_{2V}$  and  $C_{S}$  symmetries) is studied using high-level ab initio calculations. Extrapolation to the infinite basis set limit using CCSD(T)/cc-pVXZ (X = 2, 3, 4 and 5) give the energy difference as 1.6 kcal/ mol, with the  $C_{2V}$  structure lying lowest. Triple excitation contribution to the electron correlation effect and large basis sets are found to be very important. The locations of the two states on the potential energy hyper-surface are obtained to show that they represent well-defined and stable isomers.

© 2005 Elsevier B.V. All rights reserved.

#### 1. Introduction

Because of the technological interest associated to III-V semiconductors there has been interest in aluminum-phosphorus systems [1-3]. One natural question has been when the bulk properties emerge from increasing cluster sizes [4-10]. In the course of these theoretical studies, neutral AlP<sub>3</sub> appeared as a very interesting molecular system. It has been first suggested to have a triplet ground state in a pyramidal structure (C<sub>3V</sub> symmetry) [11]. Further theoretical studies [12] have suggested that, in fact, the ground state is singlet in a  $C_{2V}$ or C<sub>S</sub> symmetry lying considerably lower (at least 12 kcal/mol) than the proposed  $C_{3V}$  structure. These two  $C_{2V}$  and  $C_S$  structures (Fig. 1) were found to be very close in energy with the  $C_{2V}$  lying lowest by less than 1.5 kcal/mol [12]. This is the same situation found for AlAs<sub>3</sub> [13] where the  $C_{2V}$  state lies lower than a nearby C<sub>S</sub> state but is reversed compared to GaP<sub>3</sub> [14]. Recent theoretical studies [15,16] corroborated this picture discarding the  $C_{3V}$  structure in favor of a  $C_{2V}$  lying lower than the  $C_S$  by a slightly larger energy difference of  $\sim$ 2.5 kcal/mol. The precise characterization of the rela-

E-mail address: canuto@if.usp.br (S. Canuto).

tive energy location of the  $C_{2V}$  and  $C_S$  states is still subjected to uncertainty. Hence, high-order and wellbalanced calculations are now timely and relevant. In this Letter, we aim at obtaining an accurate determination of the relative energy of these two isomers. We first analyze the electron correlation effects quantifying the role of different contributions to the relative energy. Next, very accurate energy difference is obtained using the coupled-cluster theory with extrapolation of the correlation-consistent basis set to the infinite limit. The locations of the two states on the complex energy hyper-surface are obtained to show that the two states are localized and represent stable and independent isomers.

#### 2. Theoretical methods

Geometry optimizations are performed using MP2/ aug-cc-pVTZ and B3LYP/cc-pVTZ. In every case reported here true energy minima were obtained. To systematically analyze the role of the electron correlation effects post Hartree–Fock (HF) methods are used in the optimized structures ranging from MP2 to CCSD(T). In addition, to have a supplementary view, we also use the Brueckner orbital method [17] at the

<sup>\*</sup> Corresponding author. Fax: +55 11 3091 6831.

<sup>0009-2614/\$ -</sup> see front matter © 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.cplett.2005.06.007



Fig. 1. AlP<sub>3</sub> in the  $C_{2V}$  (left) and  $C_S$  (right) symmetries. In the  $C_S$  symmetry P3 is out-of-the-plane formed by Al1, P2 and P4.

BD and BD(T) levels. These methods are described and compared in [18]. Also, DFT calculations using different exchange-correlation functionals are used including the B3LYP [19,20] and B3PW91 [19,21]. Hybrid functionals and the nomenclature are explained in [22]. Different basis sets are used ranging from conventional to correlation-consistent cc-pVXZ (X = 2, 3, 4 and 5) gaussian-type basis functions [23]. All calculations are made using the GAUSSIAN 03 program [24].

#### 3. Discussion of the results

We first analyze the role of the different contributions to the electron correlation effects. Table 1 shows the corresponding energies obtained for the two structures using

Table 1

Total energies (hartree) with zero point vibration corrections calculated with aug-cc-pVTZ basis set over the MP2/aug-cc-pVTZ optimized geometry, for the singlet states of AlP<sub>3</sub> in the  $C_8$  and  $C_{2V}$  symmetries

Е	Cs	C <sub>2V</sub>	$\frac{\Delta E (C_{2V} - C_S)}{\text{kcal/mol}}$
HF	-1264.1572171	-1264.1565942	0.39
HFS	-1257.3213006	-1257.3214092	-0.07
SP86	-1259.8034776	-1259.8043451	-0.54
BVWN	-1269.8166008	-1269.8177665	-0.73
B3LYP	-1266.6046906	-1266.6057792	-0.68
B3PW91	-1266.4103516	-1266.4108774	-0.33
MP2	-1264.6798919	-1264.6822425	-1.48
MP3	-1264.6956707	-1264.6971417	-0.92
MP4D	-1264.7177077	-1264.7178759	-0.11
MP4DQ	-1264.6885266	-1264.6876364	0.56
MP4SDQ	-1264.6955574	-1264.6952812	0.17
MP4SDTQ	-1264.7470860	-1264.7486926	-1.01
CCSD	-1264.6946365	-1264.6937698	0.54
CCSD(T)	-1264.7400128	-1264.7401730	-0.10
BD	-1264.6931970	-1264.6922528	0.59
BD(T)	-1264.7400034	-1264.7402057	-0.13
G3	-1265.933553	-1265.9341183	-0.36

G3 uses default method basis set.

the geometry optimized at the MP2/aug-cc-pVTZ after correcting for the difference in zero-point energy vibrations. At the HF level the C<sub>S</sub> structure is more stable than  $C_{2V}$ . Accurate results require inclusion of the electron correlation effects. All DFT methods obtain the C<sub>2V</sub> as more stable and this is in agreement with MP2. Now we analyze the highest orders. At the full fourth-order MP4, with inclusion of all single, double, triple and quadruple excitations, the  $C_{2V}$  state is found to be lower by 1.01 kcal/mol. However, at the CCSD level the opposite is obtained. We should note the contribution of triple-excitations. In fourth-order it is obtained from the difference between the full MP4-SDTQ and the incomplete MP4-SDQ. It is seen to be important changing the relative stability from 0.17 to -1.01 kcal/mol. The importance of triple excitation can also be seen in larger orders where it is also decisive. For instance, the CCSD prediction is changed after including the triple excitation in CCSD(T). A similar pattern is obtained using the Brueckner orbital method. The  $C_{2V}$  structure is more stable only after including the triple excitation. The highest-level calculations, e.g. CCSD(T) or BD(T), give a relative stability of ca. 0.1 kcal/mol in favor of the  $C_{2V}$  symmetry. This energy difference is indeed very small but systematic for all high-order levels. As another estimate, the result obtained with the G3 method [25], also shown in Table 1, is similar with a relative stability in favor of the  $C_{2V}$ structure of -0.36 kcal/mol. The B3PW91 value is -0.33 kcal/mol, close to the G3 estimate. It is difficult to establish an association between any DFT result and the hierarchy of the post HF methods. But we note that the DFT methods favor the C<sub>2V</sub> structure even in the LDA approximation.

For higher level results we consider the role of basis sets effects using the correlation-consistent basis sets and extrapolating to the basis set limit. Table 2 shows the relative energies between C<sub>2V</sub> and C<sub>S</sub> structures obtained by single point calculations and extrapolations made over C<sub>2V</sub> and C<sub>S</sub> structures optimized at the B3LYP/cc-pVTZ level. It has been discussed before that this gives very good approximations to the exact structures [26]. Again, all results given were corrected for the difference in zero point vibration energies. For all theoretical levels, using the ccpVDZ basis set is insufficient for a good description of the relative energy leading that the C<sub>S</sub> structure is the lowest energy state, in contrast with our results presented in Table 1. Using the cc-pVTZ basis set, the results change for a negative sign, i.e., the  $C_{2V}$  structure is found to be more stable than the C<sub>S</sub> structure, except for the CCSD method. The failure of the CCSD reiterates that triple excitations are important to decide the issue. It is now interesting to extrapolate the results obtained for the cc-pVXZ basis to the infinite limit. For the density functional results we extrapolate the energy directly using the same scheme successfully used before [27]  $E_X = E_{\infty} + A_3 X^{-3} + A_5 X^{-5}$ . The relative energies are found in Table 2

Relative energies (kcal/mol),  $\Delta E = E_{C_{2V}} - E_{C_S}$  in various theoretical levels and extrapolated energies including correction to the difference in zero point vibrations, obtained using the B3LYP/cc-pVTZ optimized geometries

$\Delta E$ (kcal/mol)	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	Extrapolation
B3LYP	1.68	-0.48	-1.19	-2.10	$-2.45^{a}$
B3P86	1.12	-0.77	-1.32	-1.96	$-2.22^{a}$
HCTX	0.78	-0.94	-1.86	-2.10	$-2.56^{a}$
B3PW91	1.34	-0.45	-0.64	-1.71	$-1.81^{a}$
MP2	0.51	-0.97	-2.06	-2.39	-2.43 <sup>b</sup>
CCSD	3.16	0.61	-0.62	-0.90	$-0.91^{b}$
CCSD(T)	2.15	-0.15	-1.30	-1.55	-1.57 <sup>b</sup>

<sup>&</sup>lt;sup>a</sup> Ref. [27]. <sup>b</sup> Ref. [29].





Fig. 2. Extrapolation to the basis set limit of the relative energy of the two isomers using CCSD(T)/cc-pVXZ.

the range between 2.56 and 1.81 kcal/mol depending on the exchange-correlation functional used. But they all favor the C<sub>2V</sub> structure. For the MP2, CCSD and CCSD(T) there are several prescriptions for extrapolating to the basis set limit [28–31]. In one, proposed by Truhlar [28], the basis set limit for the total energy is obtained using cardinal numbers X = 2 and 3. The values obtained in this scheme were less then the values obtained using the largest cc-pV5Z basis set. Another extrapolation scheme,  $E_{\infty}^{\text{cor}} = E_X^{\text{cor}} (1 - 2.4X^{-3})^{-1}$ , was proposed by Varandas [29] and allows the use of larger cardinal numbers. The values obtained using this extrapolation scheme were based on the cc-pV5Z results and are reported in Table 2. At the highest level considered, CCSD(T), the extrapolation to the basis set limit shows that the  $C_{2V}$  state is lower in energy than the C<sub>S</sub> state by 1.6 kcal/mol. The CCSD(T) values, as a function of the cardinal number X, are shown in Fig. 2. The prescription suggested in [30] for the extrapolation of the connected triple excitations is in very good agreement with our explicitly calculated values.

The results presented above demonstrate the existence of two nearly degenerate structures, corresponding to  $C_{2V}$  and  $C_{S}$  symmetries. Table 3 gives, the calculated geometry and rotational constants of both structures obtained with MP2/aug-cc-pVTZ and B3LYP/cc-pVTZ calculations. To obtain a better understanding of the location of the two states in the energy hyper-surface. Fig. 3 shows the energy as a function of the Al-P3 distance and Al-P2-P4-P3 dihedral angle. The two states do not simply convert into one another by changing directly the dihedral angle. They have short  $(C_{2V})$  and long ( $C_{S}$ ) diagonal Al-P3 distances, with oblate-like and prolate-like characteristics. The states are well localized and correspond to two independent and stable isomers. The large interconversion barrier and the very

Table 3

Optimized distances (Å) and angles (degree) and rotational constants (MHz) for the C<sub>S</sub> and C<sub>2V</sub> singlet states of AlP<sub>3</sub>, obtained using MP2/aug-ccpVTZ and B3LYP/cc-pVTZ models

Parameter	Cs		C <sub>2V</sub>	
	MP2	B3LYP	MP2	B3LYP
R (Al–P4)	2.425	2.453	2.339	2.304
<i>R</i> (Al–P3)	3.105	3.154	2.453	2.463
<i>R</i> (P2–P3)	2.118	2.107	2.077	2.097
θ (P2–A1–P4)	60.8	60.1	102.6	104.1
θ (P2–P3–P4)	70.8	71.4	123.1	120.1
α (Al-P2-P4-P3)	108.4	110.2	180.0	180.0
Rotational constants	3899.5	3938.0	5777.4	5757.9
	2873.6	2822.8	2448.1	2471.0
	2170.6	2125.2	1719.5	1729.0



Fig. 3. The location of the two isomers of AlP<sub>3</sub>.

small energy difference between the two minima makes both isomers of interest and likely to be equally abundant.

### 4. Summary and conclusions

The relative stability of the two lowest singlet states of AlP<sub>3</sub> ( $^{1}A_{1}$  in C<sub>2V</sub> and  $^{1}A'$  in C<sub>8</sub> symmetries) has been studied theoretically. Using high-level correlated methods with large basis sets we find a very small energy difference but systematically in favor of the  $C_{2V}$ symmetry. Extrapolation to the basis set limit using CCSD(T)/cc-pVXZ (X = 2, 3, 4 and 5) gives the relative energy difference as 1.6 kcal/mol. Analyzing the different contributions to the electron correlation effects we note that the relative stability crucially depends on large basis sets and the inclusion of triple excitations relative to the Hartree-Fock reference state. The locations of the two states on the energy hyper-surface are obtained and show that they are independent and well localized representing stable isomers of similar interest.

## Acknowledgement

This work has been partially supported by CNPq and FAPESP (Brazil).

# References

- [1] C.C. Arnold, D.M. Neumark, J. Chem. Phys. 99 (1993) 3353.
- [2] C.C. Arnold, D.M. Neumark, J. Chem. Phys. 100 (1994) 1797.
- [3] G.R. Burton, C. Xu, C.C. Arnold, J. Chem. Phys. 104 (1996) 2757.
- [4] V.E. Bazterra, O. Oña, M.C. Caputo, M.B. Ferraro, P. Fuentealba, J.C. Facelli, Phys. Rev. A 69 (2004) 053202.
- [5] S. Li, R.J. Vanzee, W. Weltner, J. Chem. Phys. 100 (1994) 7079.
- [6] K. Balasubramanian, Chem. Phys. Lett. 171 (1990) 58.
- [7] U. Meier, S.D. Peyerimhoff, F. Grein, Z. Phys. D 17 (1990) 209.
- [8] P. Piquini, A. Fazzio, S. Canuto, Z. Phys. D 33 (1995) 125.
- [9] W. Andreoni, Phys. Rev. B 45 (1992) 4203.
- [10] S.C. O'Brien, Y. Liu, Q. Zhang, J.R. Heath, F.K. Tittel, R.F. Curl, R.E. Smalley, J. Chem. Phys. 84 (1986) 4074.
- [11] P.Y. Feng, K. Balasubramanian, Chem. Phys. Lett. 301 (1999) 458.
- [12] E.F. Archibong, S.K. Goh, D.S. Marynick, Chem. Phys. Lett. 361 (2002) 214.
- [13] H.K. Quek, Y.P. Feng, C.K. Ong, Z. Phys. D 42 (1997) 309.
- [14] E.F. Archibong, E.N. Mvula, Chem. Phys. Lett. 391 (2004) 325.
- [15] H. Wu, L. Guo, Z. Jin, J. Mol. Struct., Theochem. 683 (2004) 43.
- [16] L. Guo, H. Wu, Z. Jin, J. Mol. Struct., Theochem. 684 (2004) 67.
- [17] K.A. Brueckner, Phys. Rev. 96 (1954) 508.
- [18] K. Raghavachari, Annu. Rev. Phys. Chem. 42 (1991) 615.
- [19] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [20] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
- [21] J.P. Perdew, Y. Wang, Phys. Rev. B 45 (1992) 13244.
- [22] W. Koch, M.C. Holthausen, A Chemists Guide to Density Functional Theory, Wiley-VCH, Weinheim, 2001.
- [23] R.A. Kendall, T.H. Dunning Jr., R.J. Harrison, J. Chem. Phys. 96 (1992) 6796.
- [24] M.J. Frisch et al., GAUSSIAN-03, Revision B.04, Gaussian Inc., Pittsburgh, PA, 2003.
- [25] L.A. Curtiss, P.C. Redfern, K. Raghavachari, V. Rassolov, J.A. Pople, J. Chem. Phys. 110 (1999) 4703.
- [26] E.F.C. Byrd, C.D. Sherrill, M. Head-Gordon, J. Phys. Chem. A 105 (2001) 9736.
- [27] B.J.C. Cabral, S. Canuto, Chem. Phys. Lett. 406 (2005) 300.
- [28] D.G. Truhlar, Chem. Phys. Lett. 294 (1998) 45.
- [29] A.J.C. Varandas, J. Chem. Phys. 113 (2000) 8880.
- [30] E.F. Laschuk, P.R. Livotto, J. Chem. Phys. 121 (2004) 12146.
- [31] J.S. Lee, Theor. Chem. Acc. 113 (2005) 87.