

# Heavy periodane

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**Abstract** The potential energy surface of the hypothetical NaMgAlSiPSCl system (heavy periodane) is exhaustively analyzed via the gradient embedded genetic algorithm (GEGA) in combination with density functional theory (DFT) computations. The electronegativity differences among the elements in both the second and third rows of the periodic table indicate that low-energy heavy periodane structures are obtained when highly electronegative and electropositive elements are bound together, but the global minimum of the heavy periodane system is completely different to its second-row analog (LiBeBCNOF).

**Keywords** Potential energy surface · Mindless chemistry · Stochastic search · Periodane

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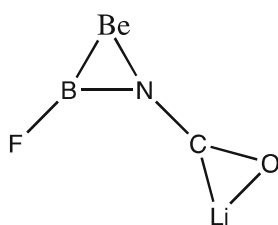
## Introduction

Periodane is a molecule that contains one atom of every element except for neon in the second period of the periodic table. Predicting the lowest-energy form of LiBeBCNOF is not easy because the potential arrangements are not obvious. In 2006, Krüger suggested that **A** is the most viable form [1]. One year later, Bera et al. explored its potential energy surface using a stochastic searching algorithm [2]. They found 27 new isomers that were substantially lower in energy than **A**. The global minimum **B** was predicted to be 122 kcal mol<sup>-1</sup> more stable [at the B3LYP/6-31 G(d) level] than Krüger's structure. Clearly, this molecule is a fleeting or viable system, but it is hard to imagine it in a bottle. Beyond the stability of periodane, this system is a nice example of "mindless chemistry" (a term coined by Bera

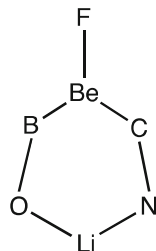
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et al. for the localization of minimum energy structures using a stochastic search where no chemical intuition is applied at all). New, exotic molecules like the title system are not studied merely due to curiosity; they are studied to demonstrate the limits of, to learn about, and eventually to understand chemical bonding and structural patterns.



A



B

Let us consider the heavier periodane congener NaMgAl-SiPSCl. Despite the constant comparison between second- and third-row chemistry, both experimental and theoretical studies illustrate structural differences between the compounds derived from both rows. For instance, it is perceived that unsaturation is strongly disfavored for the third-row species. Thus, predicting the structure of heavy periodane is again not a simple task.

In the work described in this manuscript, we explored the potential energy surface (PES) of heavy periodane using the gradient embedded genetic algorithm (GEGA) proposed by Alexandrova [3, 4]. Interestingly, the electronegativity differences among the elements in both the second and third rows indicate that low-energy heavy periodane structures are obtained when highly electronegative and electropositive elements are bound together, but the global minimum of the title system is completely different to that of its second-row analog. From a computational point of view, heavy periodane is also interesting because its potential energy surface is extremely rough, making it attractive for testing the limitations of stochastic searching algorithms.

### Methodology and computational details

Several population-based optimization heuristics have been devised for global minimum searching in chemistry [5]. Some of them are the well-known simulated annealing method [6] (or modified versions) [7], particle swarm optimization [8], big bang–big crunch [9], the basin-hopping method [10, 11], the kick technique [12], multicanonical methods [13], and minima hopping [14]. However, none of these methodologies provides a universal optimization

strategy (a strategy capable of solving all optimization problems). In our case, we used the GEGA program to search for the global minimum structure. In GEGA, data recombination (molecular substructure combination in the genetic crossover) provides a good compromise between data conservation and exploration. Every structure involved in the genetic algorithm procedure is checked to ensure that it is a local minimum through geometry optimization and vibrational frequency analysis. GEGA has proven to be exceptionally successful at finding the global and the low-energy local minima on the PESs of atomic clusters [15–25]. Readers who wish to delve more deeply into the details of this algorithm are referred to Ref. [18].

In this study, all GEGA computations were performed using the PBE0 [26] functional with the LANL2DZ [27] basis set. The initial population was 10, and the numbers of germinal linear, two-dimensional, and three-dimensional individuals were fixed at 20 each. The mating and mutation cycle converged when the lead structure had stayed the same for ten iterations. The GEGA search was repeated five times to ensure that the result was reproducible. All of the GEGA structures were subsequently reoptimized using the same functional but in conjunction with a def2-TZVP [28] basis set. The PBE0 functional has been shown to provide accurate structural results and satisfactory values for thermodynamical, kinetic, and spectroscopic properties across the whole periodic table [26]. Nevertheless, to guarantee that the global minimum structure is not an artifact of the selected methodology, all geometries were reoptimized in different density functional approaches (BLYP, PW91, M06, and TPSSh) using the same basis set (def2-TZVP). All of the selected functionals gave similar structural parameters. A final evaluation of the relative energies calculated at the CCSD(T)/def2-TZVP//PBE0/def2-TZVP level was used to identify the lowest-energy isomer. The nature of the stationary points and the zero point energy corrections were examined by calculating the Hessian matrix at the same level as the optimizations. All geometry and energy refinement computations were done using Gaussian 09 [29].

### What is the most stable isomer of heavy periodane?

Table 1 summarizes the energy differences, including the zero point energy corrections, obtained using the distinct functional approaches and the energy evaluations performed at the CCSD(T)/def2-TZVP//PBE0/def2-TZVP level of theory. Some general trends can be seen in Table 1. (i) The first two minima persist at all levels of theory. (ii) The energy gap between structures **1** and **2** is between 3 and 4 kcal mol<sup>-1</sup>. (iii) PBE0, TPSSh, and PW91 yield quite similar energy differences. Therefore, for the rest of this discussion, we will focus our attention on the PBE0 results.

**Table 1** Energy differences (in kcal mol<sup>-1</sup>) computed at different levels of theory. All computations were performed using the def2-TZVP basis set. The smallest vibrational frequency (in cm<sup>-1</sup>) is shown in parentheses

Structure	PBE0	BLYP	PW91	M06	TPSSh	CCSD(T)//PBE0
<b>1</b>	0.0 (52)	0.0 (49)	0.0 (49)	0.0 (45)	0.0 (52)	0.0
<b>2</b>	4.1 (21)	3.7 (19)	4.0 (22)	3.3 (22)	4.1 (17)	3.5
<b>3</b>	6.7 (60)	8.3 (59)	6.8 (58)	8.4 (58)	6.7 (60)	7.6
<b>4</b>	7.0 (27)	5.6 (27)	6.3 (26)	6.1 (26)	7.8 (26)	7.0
<b>5</b>	8.4 (26)	8.5 (30)	7.2 (23)	7.3 (24)	9.0 (25)	8.2
<b>6</b>	10.9 (20)	11.3 (21)	10.8 (22)	11.0 (26)	11.1 (20)	11.1
<b>7</b>	12.5 (31)	7.3 (32)	11.0 (27)	<sup>a</sup>	13.5 (31)	10.9
<b>8</b>	12.7 (18)	4.6 (17)	10.2 (18)	9.4 (28)	12.0 (20)	8.3
<b>9</b>	12.7 (16)	9.8 (10)	11.2 (13)	11.8 (16)	13.1 (15)	13.2
<b>10</b>	13.9 (18)	5.0 (19)	11.9 (17)	10.0 (27)	13.6 (19)	8.2

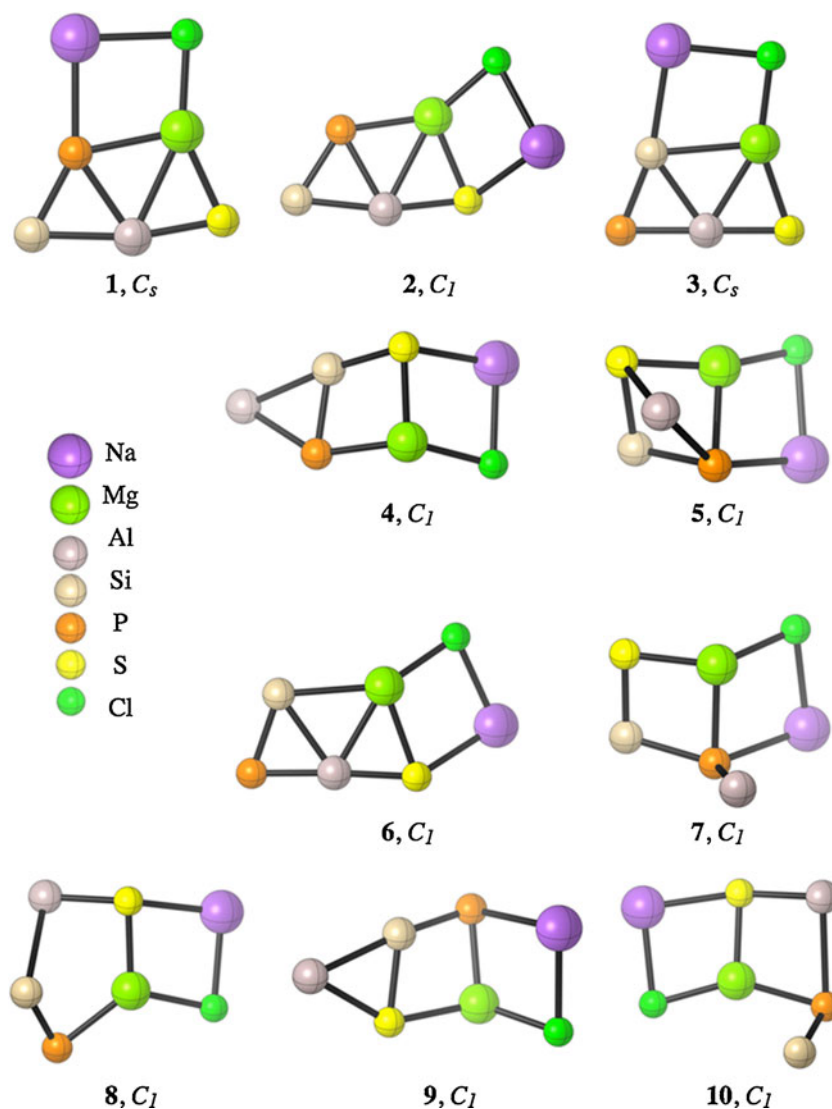
<sup>a</sup>At the M06/def2-TZVP level, structure 7 converges to 5

Ten local minimum structures are found within 15 kcal mol<sup>-1</sup> of the global minimum when the PBE0 functional is used in conjunction with the def2-TZVP basis set (see Fig. 1). It is important to note that all of the structures in Fig. 1 and Table 1

are singlets. The lowest-energy triplet form is 18.3 kcal mol<sup>-1</sup> higher in energy than **1** at the PBE0/def2-TZVP level.

We expected that, as in periodane, the most stable forms involve interactions between electronegative and electropositive

**Fig. 1** Lowest-lying isomers of heavy periodane. Geometries were computed at the PBE0/def2-TZVP



atoms. The most obvious motifs are Na–Cl and Mg–Cl or a combination of both (Na–Cl–Mg); indeed, the latter triad emerges in all ten lowest-lying arrangements. The other apparent motif is Mg–S, which is present in every structure in the top ten depicted in Fig. 1. Another fragment that is manifested in five of the first six heavy periodane isomers is the triangle Si–P–Al. In the 20 lowest-energy periodane isomers reported by Bera et al., the C–N and B–O units occur regularly. Similarly, the heavy counterparts of C–N and B–O, namely Si–P and Al–S, are recurrent motifs in the lowest-lying isomers of heavy periodane: the Si–P dyad appears in the ten lowest-energy isomers reported, while the Al–S motif emerges in eight of them (**4** and **7** are the only exceptions). Clearly, although the electronegativity differences in the third period are not as large as those in the second period, low-energy heavy periodane structures are obtained when highly electronegative and electropositive elements are bound together. Therefore, some patterns of the heavy periodane forms are conceivable in principle, but it is still hard to think of all potential isomers.

Our computations reveal that the lowest-energy isomer is the singlet planar structure **1**, which is completely different to the periodane one (**B**) [2]. Vibrational analysis of **1** shows that the lowest-energy mode of the cluster is  $52\text{ cm}^{-1}$  (computed at the PBE0 level), and this soft mode involves the displacement of the P–Mg dimer out of the molecular plane. Note that **1** contains an aluminum atom surrounded by a Si–P–Mg–S moiety, where the Na–Cl dimer interacts with the P–Mg flank. The second most stable form, **2**, is  $4.1\text{ kcal mol}^{-1}$  higher in

energy than **1**. It has the same Si–P–Mg–S core, but the Na–Cl unit is bound to the Mg–S side. The third most stable isomer is quite similar to **1**, but the Si and P atoms are switched.

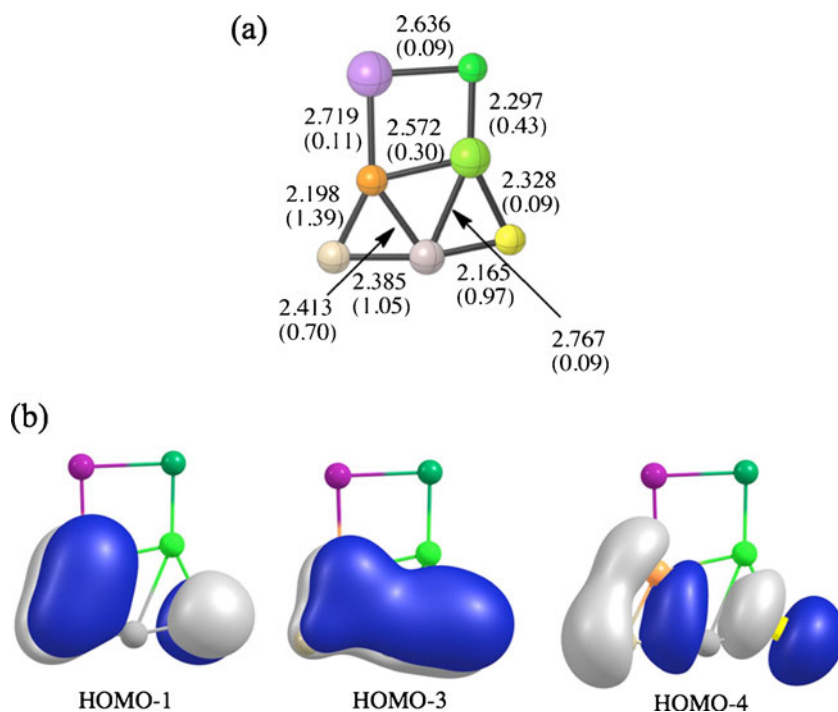
## Bonding

The structural parameters and Wiberg bond indices (WBIs) for isomer **1** are summarized in Fig. 2a. The NPA charges show that the two elements with strong cationic character (Na,  $+0.88$  and Mg,  $+1.20$  |e|) are intercalated between the Cl ( $-0.70$  |e|), P ( $-1.24$  |e|), and S ( $-1.02$  |e|) atoms. The remaining atoms, Si and Al, have positive charges ( $+0.11$  and  $+0.77$  |e|, respectively). Actually, two different fragments can easily be discerned; the first is a distorted square P–Na–Cl–Mg moiety with strong ionic character, while the second is a linear Si–Al–S moiety that is mostly covalent.

The Si–P bond length ( $2.198\text{ \AA}$ ) is shorter than the single Si–P bond length of silylphosphine determined by microwave spectroscopy ( $2.25\text{ \AA}$ ) [30]. The Al–S distance in heavy periodane ( $2.165\text{ \AA}$ ) is also very short. Guha and Francisco reported an Al–S bond length of  $2.249\text{ \AA}$  for AlSH, calculated at the CCSD(T)/aug-cc-pV5Z level of theory, and attributed multiple character to the Al–S interaction [31]. Therefore, it looks like our title system has Si–P and Al–S multiple bonds. Clearly, the  $\pi$  orbitals are mostly located around the P–Si and Al–S units (Fig. 2b), confirming the multiple-bonding nature of these interactions.

WBIs confirm the existence of two units, one of them strongly ionic (PNaClMg) with small WBI values ( $<0.5$ ),

**Fig. 2** **a** Selected geometrical data (in  $\text{\AA}$ ) and Wiberg bond indices (in parentheses) of heavy periodane. **b** Selected MO of heavy periodane. Contours represent  $0.03\text{ au}$



and a second with a strong covalent character (Si–Al–S) and WBI values of  $>0.97$ . Clearly, while the P–Al interaction has a significant covalent contribution, the Al–Mg one is more ionic (WBI=0.09).

Finally, note that HOMO-3 is delocalized around the P–Si–Al–S core, but the geometrical parameters indicate localization. Therefore, in order to gain further insight into the electron delocalization in heavy periodane, the induced magnetic field  $\mathbf{B}^{\text{ind}}$  [32, 33], a magnetic descriptor of aromaticity, was computed. The  $z$  component of  $\mathbf{B}^{\text{ind}}$  ( $B_z^{\text{ind}}$ ) indicates only minor delocalization. The most delocalized region is found at the P–Si–Al triangle, with a  $B_z^{\text{ind}}$  value of  $-5.6$  ppm.

## Conclusions

We found that the ten most stable isomers of periodane had well-defined patterns involving interactions between electronegative and electropositive atoms. In principle, some of the candidates for the global minimum structure could be proposed on paper, but it would require too much effort to accurately pinpoint it. The putative lowest-energy isomer is planar, with two highly recognizable fragments—the strongly ionic PNaClMg square and the mainly covalent Si–Al–S triad. The multiple-bonding character of the Si–P and Al–S bonds is also remarkable.

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