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Cluster simulations of structural transformations in yellow arsenic

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Yellow arsenic (y-As) consists of tetrahedral As_4 molecules that may be packed in some amorphous and crystalline structures. Like many other arsenic structures, y-As is metastable and undergoes irreversible transitions (polymerization) under irradiation. The process of y-As polymerization, which is observed experimentally, usually leads to the formation of amorphous arsenic (a-As) possessing a continuous random network structure. Our previous quantum chemical simulation for an eight-atom cluster model performed using semi-empirical CNDO/BW approach, combined with optimization technique of cyclic coordinate descent, have shown a formation of molecular dimers due to breaking of one bond in each tetrahedral As_4 molecule accompanied with bond switching over to chair-like structure. In that case a pair of approaching As_4 molecules is positioned in a staggered "face-to-face" configuration (D_{2d} symmetry), which may be considered as a conformation with a six-membered chair-shaped ring dominating in the structure of a polymerized a-As. Two energetically preferable configurations of an As_8 cluster have been found here after careful semi-empirical optimization of the face-to-face structure: they possess either cubane configuration (O_h symmetry) or eclipsed "edge-to-edge" configuration (D_{2h} symmetry). For the first time, a two-dimensional energy surface $E(z, \theta)$ has been calculated in order to analyze possible paths of structural transformations in y-As. Analogous qualitative results have been just obtained by us when using ab initio Hartree–Fock method combined with the electron correlation corrections for eight-atom cluster model of molecular arsenic. A comparison of both quantum chemical simulations, together with data from previous experimental studies allows us to describe a possible mechanism of the initial stage of the polymerization of y-As. © 2001 Elsevier Science B.V. All rights reserved.

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Scientific interest in structure and various properties of elements of the V*A* group of the Periodic Table (pnictides) has increased essentially beginning with active technological application of epitaxial semiconducting films based on two-compound III*A*–V*A* materials. In particular, a number of experimental and theoretical studies have been devoted to molecular allotropic forms of pnictides, including growth of clusters [1–17]. In the quenched vapor of phosphorus at 300 K molecular clusters P_n up to $n = 24$ were identified by Martin [1]. Theoretical studies of clusters as well as molecular crystals of P, As, Sb and Bi have been performed using various methods of quantum chemistry and molecular dynamics. Halevi et al. described dimerization of molecular phosphorus $(2P_4 \rightarrow P_8)$ using the semi-empirical method of Modified Neglect of Diatomic Overlap (MNDO) [3]. Häser et al. [10] used the ab initio method of Self-Consistent Field (SCF) in order to simulate clusters up to $n = 28$ and proposed both the probable reaction scheme for

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the formation of red phosphorus from white phosphorus units as well as possible structural units of red phosphorus. Using density functional method combined with molecular dynamics technique, Hohl and Jones [12] simulated polymerization of 26 P_4 molecules in liquid state, which leads to the formation of a disordered phosphorus network. Transition between molecular liquid (P_4) and polymeric phosphorus has been observed recently by synchrotron radiation [18]. Ungar, et al. described theoretically both the structure and dynamics of a molecular crystal of white phosphorus (β-P_4) [15]. The structure and electronic properties of arsenic, antimony and bismuth clusters have been also simulated using various theoretical methods [4,7,11,13,14]. In particular, Ballone and Jones [11] using a method, which is based on the Density Functional Theory combined with Molecular Dynamics (DFT/MD), optimized some equilibrium configurations for various As_n clusters, where n successively changed from 2 up to 11, and compared them with analogous P_n clusters.

Technological importance of yellow arsenic (y-As) has been discussed in more detail in our review paper [19]. Depending on the temperature, pressure and preparation conditions, y-As may exist in several crystalline and amorphous states, all structural units contain tetrahedral As_4 molecules only [20]. Various modifications of y-As are unstable. Under the light illumination in a visible region, irradiation by UV, X-rays, and energetic particles, as well as heating, the molecular structure of y-As suffers irreversible changes. They lead to a bond switching between the As_4 molecules and further formation of a network of covalent bonds in amorphous arsenic (the polymeric state of a-As). The polymerization of y-As presents a multistage process. The starting stage of molecular cluster formation is of particular interest, namely the study of the reaction pathway of the interaction among tetrahedral As_4 molecules. Recently we have studied experimentally and theoretically various molecular modifications of y-As and their structural transformations [19–24]. The details of the initial stage of polymerization have not been quite clear up to now. In Refs. [22–24] we have proposed a basic path of the polymerization reaction in y-As. The process starts by an interaction between two As_4 molecules. A characteristic structural property of the a-As network is the existence of poly-membered rings. In particular, the weight proportion of six-membered rings, predicted by the Greaves and Davis model [25], is high and equals 22%. Moreover, in the interaction of As_4 molecules leading to the formation of the amorphous As network one must take into consideration the Woodward–Hoffmann principle of orbital symmetry conservation in this reaction [26]. A correlation diagram of molecular orbitals (MO) for two reacting As_4 molecules and As_8 dimer shows that the highest occupied MO of the reactant correlates with the antibonding empty MO of the product [19]. This means that the reaction is rather forbidden by symmetry in the ground state and thus may take place only through electronic activation.

Quantum chemical simulations of a symmetric eight-atom system of arsenic (two interacting As_4 molecules, equilibrium configurations of a molecular As_8 dimer, and structural transitions between them) were begun using the modified version of semi-empirical CNDO/BW code according to ideas developed by Rodionov [23,24]. The calculations have shown that in the initial polymerization stage we have a formation of As_8 dimers due to breaking of one bond in the tetrahedral As_4 molecule. Simulation of this process shows that formation of a stable As_8 cluster, possessing either D_{2h} or O_h symmetry, may take place if the dimerization path possesses the D_{2d} symmetry. For the first time we constructed here a two-dimensional energy surface $E(z,\theta)$ and analyzed in detail possible paths of the structural transformations in a molecular arsenic. To verify these calculations we used results of DFT calculations on some different symmetric As_8 clusters performed earlier by Ballone and Jones [11]. But in order to go beyond semi-empirical approach in the description of the cluster model of y-As, we have applied ab initio Hartree–Fock method being combined with a posteriori electron correlation corrections. Results of both simulations, together with data of previous studies, allow us to describe more reliably the possible mechanism of the initial stage of irreversible polymerization, which takes place in y-As.

In order to describe structural transformations in y-As, we have used the symmetric eight-atom cluster

model. Fig. 1 shows four energetically favorable configurations of this cluster obtained using computational optimization:

(a) two remote As_4 molecules with undistorted T_d symmetry (D_{3d} point group);

(b) staggered "face-to-face" chair-like dimer structure (D_{2d} point group),

(c) cubane-like configuration (O_h point group);

(d) eclipsed "edge-to-edge" dimer structure (D_{2h} point group).
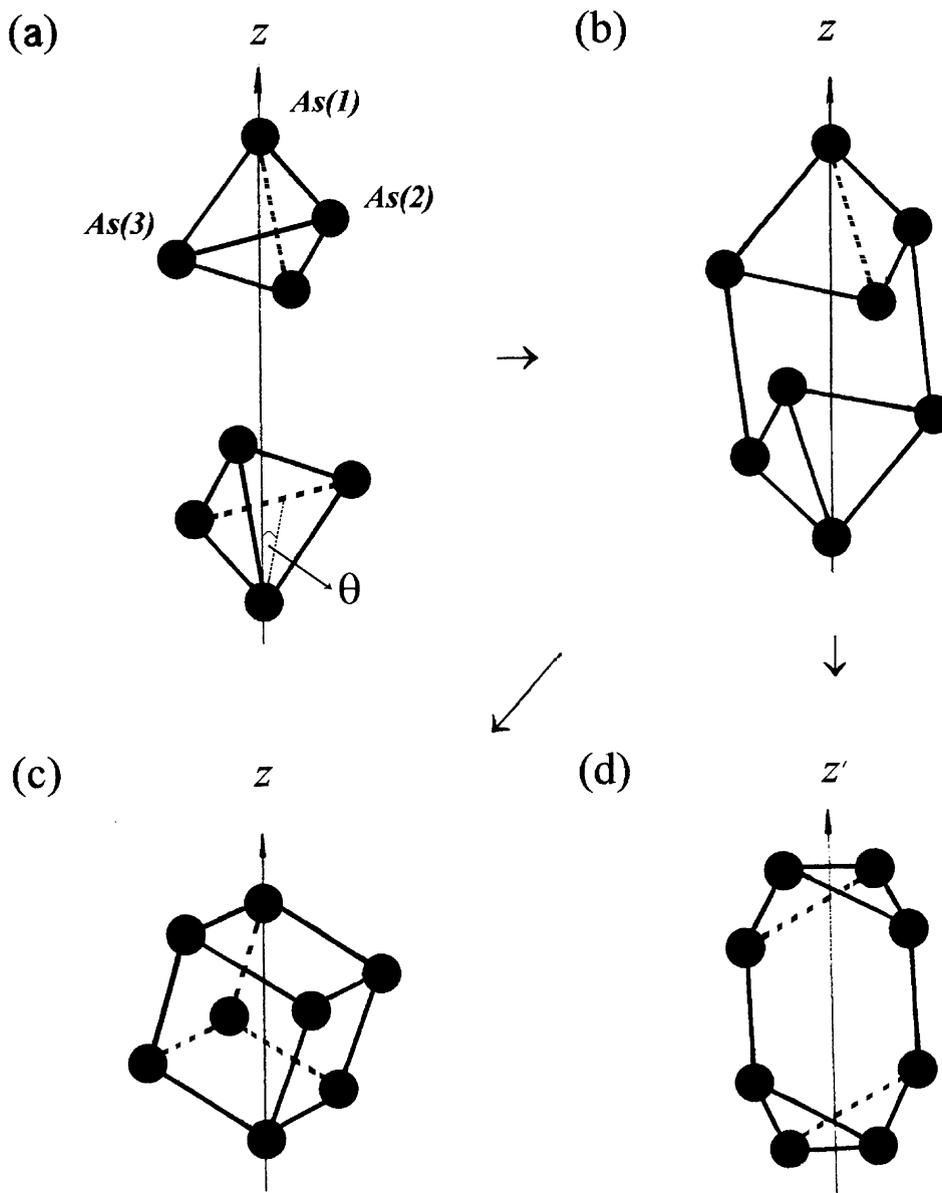

Fig. 1. Equilibrium configurations of the systems consisting of either two separated As_4 molecules (*a*) or different structures of molecular As_8 dimer (*b–d*). θ is the angle between plane As(2)–As(1)–As(3) and the z axis. Arrows indicate directions of possible structural transformations during the y-As polymerization.

Transformations $a \to b \to c$ can be done by a compression of an As_8 cluster along the z coordinate after mutual approach of As_4 molecules. Transformation $b \to d$ is possible when a z-axis, which connects opposite outermost atoms of the bounded tetrahedra, turns towards the z' direction passing through middle points of the uppermost As–As bonds of these tetrahedra. Meanwhile, one of As_8 configurations (C_{2v} point group) considered by Ballone and Jones [11] was not checked in our simulations since the path for the structural transformation in this case is too complicated. Moreover, a difference of binding energies between As_8 clusters with C_{2v} and D_{2h} symmetries was found to be rather small (0.1–0.2 eV).

For an optimization of the total energy of the As_8 cluster, the method of cyclic coordinate descent has been used [23]. Five to seven pairs of internal coordinates have been optimized independently (simultaneously for both As_4 tetrahedra) during approach of the two interacting molecules to each other. In addition to the one-dimensional scanning along the z (or z') coordinate, a similar procedure of two-dimensional scanning along a pair of coordinates has been performed. Such a simulation allowed us to obtain various energy surfaces, e.g. $\Delta E(z, \theta)$ (Fig. 2), which are suitable for detailed simulation of the reaction pathways. The corresponding trajectories shown in Fig. 2 give the simplest representation of possible pathways of structural transformations $a \to b \to c$ during the polymerization process in a molecular arsenic, which can take place under energy radiation in order to overcome the corresponding potential barriers. Figs. 3 and 4 show the energy curves corresponding to one-dimensional scanning along the z and z' coordinates, respectively. Note that $z_{As4-As4}$ and $z'_{As4-As4}$ describe the distances between the most remote apexes (Fig. 1a–c) and edges (Fig. 1d) in various eight-atom configurations, respectively. Fig. 5 presents the energy diagram for all equilibrium structures of the arsenic cluster model shown in Fig. 1 as well as transitions between them. All the calculations were performed for the ground (singlet) electronic states of various As_8 clusters. Some their configurations, which correspond to local minima or saddle points on the energy surface, have also been re-calculated in the triplet state (Table 1).

The details of semi-empirical calculations of the

As_8 cluster model have been described by us elsewhere [23,24]. To this end, we have adapted our version of the CNDO/BW code [27] developed on the base of the method of Complete Neglect of Differential Overlap combined with both the parameterization scheme of Boyd–Whitehead [28] and the optimization procedure mentioned above. It considers two main stages of operations:

- Preliminary calibration of two-center α_{XY} and β_{XY} parameters for the corresponding $X-Y$ bond of small test molecules in order to reproduce their equilibrium geometry and binding energy.
- Computational optimization of possible structures of the system under study and transition paths between them, using calculations of the total (or binding) energy for successively varying the geometry of this system (according to the method of cyclic coordinate descent).

Ab initio simulations of the structural transformations in a y-As crystal have been performed for the same model of an As_8 cluster using HF–CC method (Hartree–Fock formalism combined with a posteriori DFT electron correlation corrections). The corresponding computational scheme is implemented in the CRYSTAL95 code [29], and we have used its non-periodic, molecular regime to perform calculations. Ballone and Jones in the analysis of their DFT calculations on P_n and As_n clusters [11] concluded that exchange and correlation functionals based on Generalized Gradient Approximation (GGA) give more reliable results than those constructed using Local Spin Density Approximation (LSD). We have considered three a posteriori DFT correlations, which are implemented in CRYSTAL95: those of Perdew–Wang (PWGGA [30]) and Lee–Yang–Parr (LYP [31]), which belong to GGA scheme, and that of Vosko–Wilk–Nusair (VWN [32]), which is the typical LSD functional. Table 1 presents our main results obtained using all aforementioned methods, while in Figs. 3–5 we compare the CNDO/BW and HF–CC (PWGGA) data only. To provide an adequate comparison of energies for different computational schemes we have used relative values of ΔE, equating to zero the total energy of two remote As_4 molecules.

Due to limitations of computational resources we could not minimize the total energy of arsenic clusters
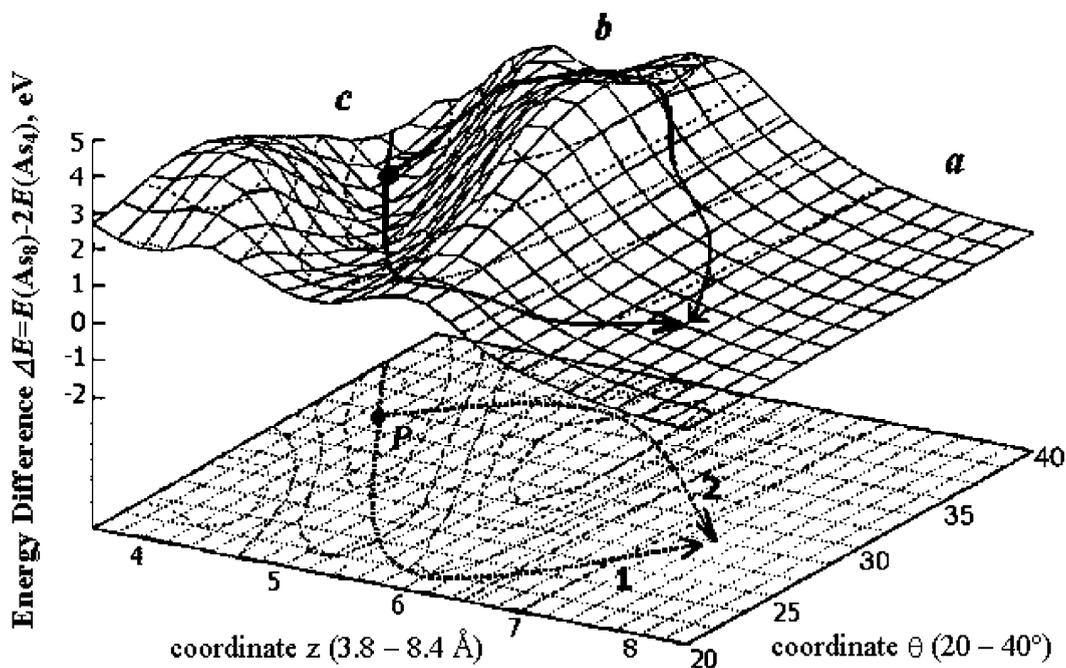
Fig. 2. Fragment of the energy surface $\Delta E(z,\theta)$ for an As_8 cluster and its topographical projection based on semi-empirical CNDO/BW calculations. Curves 1 and 2 denote two different trajectories used for ab initio HF–CC and CNDO/BW calculations (Fig. 3) containing either saddle point (1) or local minimum (2), whilst P is a projection of their crossing point. Dashed curves on $\Delta E(z,\theta)$ and their topographical projections denote energy isolines. Three areas a, b, and c refer to the corresponding As_8 structures shown in Fig. 1.
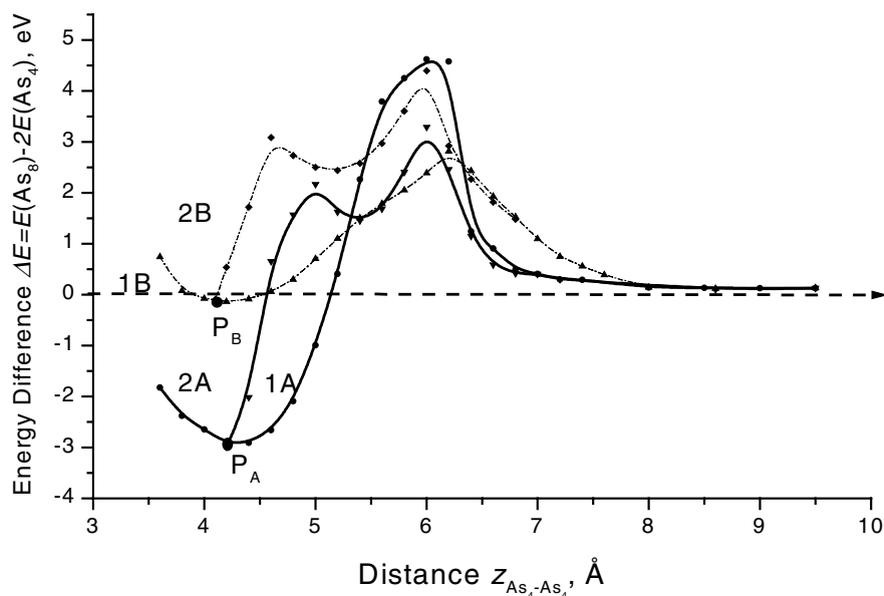

Fig. 3. Energy curves $\Delta E(z)$, calculated using HF–CC (A) and CNDO/BW (B) methods and obtained by sectioning of the energy surface $\Delta E(z,\theta)$ along the trajectories 1 and 2 (Fig. 2), which are intersecting at P_A and P_B points, respectively. The latter corresponds to P point in Fig. 2.
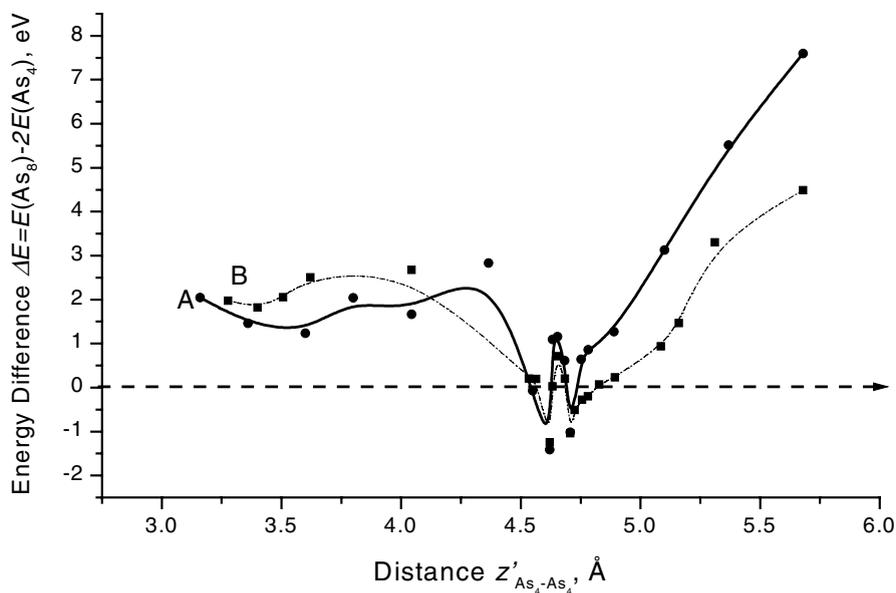
Fig. 4. Energy curves $\Delta E(z')$ for eclipsed edge-to-edge configuration of an As_8 cluster (D_{2h} symmetry group shown in Fig. 1d), calculated using HF–CC (A) and CNDO/BW (B) methods.
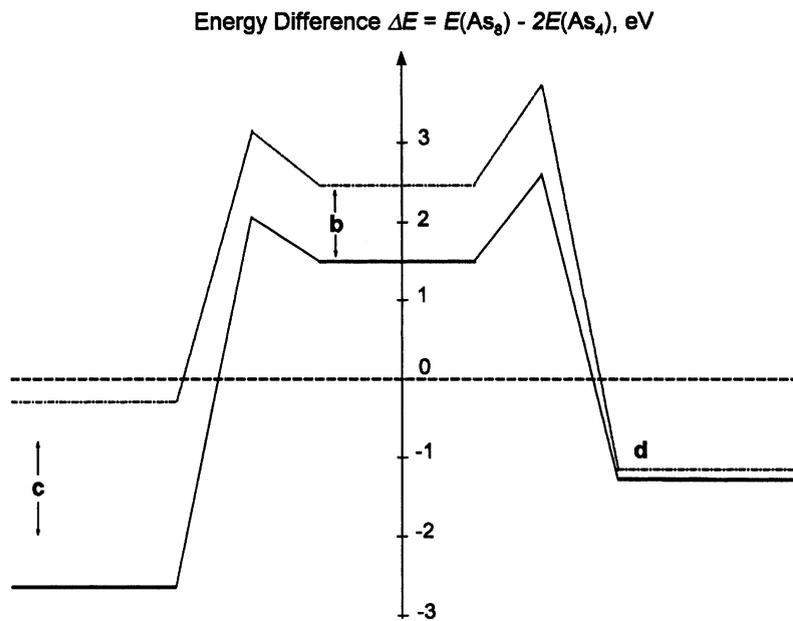

Fig. 5. Energy diagram for reaction pathways $b \rightarrow c$ and $b \rightarrow d$ (Fig. 1), calculated using HF–CC and CNDO/BW methods (solid and dash–dot lines, respectively). Intermediate energy states (bold solid line) along both pathways refer to transition structures of an As_8 cluster. The zero level (bold dashed line) on the diagram corresponds to the energy of two separated As_4 tetrahedra calculated using both methods.

Table 1

Relative energy $\Delta E(\Delta E = E(As_8) - 2E(As_4)$; since energy of As_8 configuration with two separated arsenic tetrahedra (*a*) is equated to zero it is not presented in the table) (eV) for different structures of arsenic eight-atom cluster

Method of calculation	Configurations of As_8:							
	Dimerization saddle[a]		Chair-like (*b*)		Cubane-like (*c*)		Eclipsed structure (*d*)	
	Singlet	Triplet[b]	Singlet	Triplet[b]	Singlet	Triplet[b]	Singlet	Triplet[b]
CNDO/BW	2.6	–	2.4	–	−0.2	–	−1.1	–
HF–CC (PWGGA)	3.2	0.04	1.5	−2.6	−2.9	−5.7	−1.4	−2.9
HF–CC (LYP–GGA)	3.4	0.3	1.7	−2.3	−2.6	−5.4	−1.2	−2.7
HF–CC (VWN–LSD)	3.9	0.7	2.1	−1.9	−2.2	−5.0	−0.8	−2.3
Results of DFT calculations performed by Ballone and Jones[c]								
GGA functionals	–	–	–	–	1.6	–	0.5	–
LSD functionals	–	–	–	–	0.9	–	0.2	–

[a] Configuration of As_8 cluster, which corresponds to the top of the energy barrier of dimerization (Fig. 3).

[b] Calculations on As_8 cluster in the triplet state were performed using HF–CC method; in such cases zero of energy is chosen for this state of separated As_4 molecules, the energy barrier of their excitation is ~4.4 eV.

[c] In Ref. [11], data for As_8 clusters were presented in the binding energies per atom; to keep the same format of results as shown in the table we have transformed them according to $\Delta E = E(As_8) - 2E(As_4)$.

using HF–CC method so carefully as it was done in the semi-empirical calculations, except for two most symmetric configurations of As_4 tetrahedron and As_8 cube. Thus, we have chosen both equilibrium configurations of arsenic clusters and transition paths between them described in our previous paper [24] as an initial guess, and then re-optimized them in narrow intervals of spatial coordinates when performing ab initio calculations. We have used for them the all-electron basis set (BS) 976-5d3-1G, which was suggested for arsenic by Harrison [29]. Both $3d^{10}$ and $4s^2 4p^3$ outer shells as well as $5s5p$ polarization function have been re-optimized to achieve minimum of total energy for an As_4 tetrahedral molecule. As a result of both geometry and BS optimization, the equilibrium shape of this molecule was found to be an undistorted tetrahedron with a length of edge $r_{As-As} = 2.50$ Å. It is 2.5% larger than the corresponding experimental value of 2.435 Å [33].

Since the $s^2 p^3$ valence electron configuration possesses characteristic $p\sigma$-bond angles exceeding 90° ("banana"-type strained bonds [2]), the stability of tetrahedral pnictide molecules is relatively low. The excess energy of strain in a four-atom tetrahedron

may be removed in the process of bond breaking and switching between the interacting pnictide molecules. Such a reaction pathway considered earlier for both molecular phosphorus [3] and arsenic [34], was also described in our review paper devoted to y-As [19]. According to structural data of Daniel and Leadbetter [34] the local structure, even in the disordered phase of y-As, may be successfully modeled by staggered face-to-face packing of As_4 tetrahedra (Fig. 1a). It is chosen as a starting point in our quantum chemical simulations of the reaction pathway for the initial stage of y-As polymerization. The next step includes a structural transition $a \rightarrow b$ (Fig. 1), resulting in the formation of a chair-shaped configuration of the As_8 dimer. After breaking of a pair of nearest parallel As–As bonds in both molecular tetrahedra (*a*) and further intermolecular bond switching (*b*), this configuration contains a six-atom ring. Our previous one-dimensional scanning along the *z* axis simultaneously with a structural optimization of the As_8 system using CNDO/BW code [23] has lead to the appearance of two non-coinciding energy curves $\Delta E_1(z)$ and $\Delta E_2(z)$ corresponding to the $a \rightarrow b$ and $b \rightarrow a$ transformations and crossing at a point $z_c \sim 6.2$ Å. That is a typical example of Hartree–Fock instability (HFI), which is displayed for some configurations of polyatomic systems when using semi-empirical methods neglecting reliable electron correlation. For instance, it was

also observed during MNDO simulation of the reaction pathway $2P_4 \rightarrow P_8$ [3]. The sharp peak in the vicinity of z_c allows us to estimate an energy barrier of As_8 dimerization to be ~2.6 eV at a configuration of two separated As_4 molecules preceding their coming together. In our HF–CC calculations such a barrier is even higher (Table 1) but without any signs of HFI (Fig. 3).

Direct experimental estimate of this energy barrier is rather problematic. When using the results of Differential Thermal Analysis (DTA) for y-As [22] treated by the kinetic equation of Avraami [25] the barrier of polymerization was estimated to be 0.48 ± 0.07 eV. Such a marked difference from our calculations could be caused by several reasons. Experimental temperatures inevitably reduce the height of such a barrier as compared to quantum chemical modeling, which may reproduce $T = 0$ K only. On the other hand, the real structure of y-As is either a molecular crystal or an amorphous network of As_4 molecules, where initiation of polymerization is rather a collective effect than a local one. Moreover, according to the Woodward–Hoffmann principle [26] the dimerization reaction cannot occur by symmetry in the ground (singlet) state, therefore, the transition $a \rightarrow b$ simulated by us should be meta-stable. When using the HF–CC method we have re-calculated all those As_8 configurations in the triplet state, which correspond to the local minima and saddle points on optimized energy curves (Table 1). Energy barriers for the excitation of the pair of two remote As_4 molecules (Fig. 1a), As_8 cluster corresponding to the dimerization saddle point, and the chair-like structure (Fig. 1b), are found to be 4.4, 1.2 and 0.4 eV, respectively (when using PWGGA correlation corrections). Thus, for the unstable triplet state of the As_8 cluster, transition $a \rightarrow b$ should be almost spontaneous, in accordance with the mechanism of photo-polymerization of y-As, as proposed in our earlier experimental studies [19].

We could avoid the HFI of semi-empirical calculations on the As_8 system only by performing a two-dimensional scanning with simultaneous optimization of its other internal coordinates, which allowed us to construct the energy surface $\Delta E(z,\theta)$ [24]. The choice of θ (Fig. 1a) as a second scanning coordinate was caused by its higher sensitivity to structural transformations in an eight-atom cluster as compared to other

internal coordinates. An analysis of the energy surface $\Delta E(z,\theta)$ (Fig. 2) clearly shows the two possible pathways of As_8 dimerization $a \rightarrow b \rightarrow c$ marked by the curves 1 and 2 with arrows (their opposite directions are chosen for convenience). Despite a variety of configurations for two remote As_4 tetrahedra, they possess close values of energy ($\Delta E \approx 0$) and correspond to an asymptotic flat area on the energy surface. As to the area around a left corner of the $\Delta E(z,\theta)$ surface shown in Fig. 2, it could indicate a beginning of the transition to eclipsed edge-to-edge dimer structure of As_8 (Fig. 1d), but this is not obvious here due to a very complicated change of z and θ during such structural transformation. Both paths 1 and 2 have been re-calculated using HF–CC method with a limited structural optimization of the eight-atom cluster (Fig. 3) but with different correlation functionals (Table 1). Ab initio calculations have confirmed our qualitative conclusions made earlier on the basis of the semi-empirical simulations for the As_8 cluster [24]. Moreover, the trajectory 2, which possesses a marked local energy minimum for both computational series corresponding to a chair-shaped As_8 dimer (Fig. 1b), is energetically more preferable in the HF–CC calculations. Along this path of the structural transition $b \rightarrow c$ one may observe the energy barrier 0.4–0.5 eV. At the same time, along the path *1* no minima or saddle points for the *b* configuration exist on the corresponding $\Delta E(z)$ curves, as calculated using both CNDO/BW and HF–CC methods. Thus, the energy trajectory 2 may be considered as more realistic, in accordance with the model of Daniel and Leadbetter [34].

The cubane-like *c* structure of an As_8 cluster is characterized by a marked energy minimum when performing both semi-empirical and ab initio calculations. Using the CNDO/BW code, this configuration was optimized by means of the successive decrease of the z distance along the pathway $b \rightarrow c$, with the same D_{2d} symmetry as in the case of *b* structure. In this case, an energy minimum was achieved for the cubane-like structure with a small deviation from the O_h symmetry. When using the CRYSTAL95 code we have optimized both this cubane-like configuration and the eight-atom arsenic cube (O_h point group). The latter was found to be by ~0.3 eV energetically more preferable, and energy curves corresponding to the HF–CC calculations shown in Fig. 3 include this

factor of structural re-optimization. The main difference between results of our semi-empirical and ab initio simulations on As_8 cluster is the ratio of relative energies for its a and c configurations (Table 1, Fig. 3). For the former method they are almost equal, the HF–CC calculations surprisingly showing marked energy preference for the cubane-like As_8 structure. This may probably be explained by overestimate of the As–As bond lengths in the HF calculations: equilibrium lengths of the edges for both As_8 cube and As_4 tetrahedron are practically the same (2.50 Å). In the CNDO/BW calculations, the experimental geometry of tetrahedral As_4 molecule ($r_{As–As} = 2.435$ Å) served for the calibration of two-center semi-empirical parameters, while As–As bond lengths in the cubane-like As_8 cluster were found to be larger by 1–1.5%.

To optimize the structure of the eclipsed edge-to-edge As_8 dimer configuration (Fig. 1d) in CNDO/BW calculations we have simultaneously combined the one-dimensional scanning along the z' coordinate, with optimization of other internal coordinates (Fig. 4). The energy curves $\Delta E(z')$, calculated using both CNDO/BW and HF–CC methods, qualitatively agree, even the splitting of energy minima almost coincide. We suggest that the presence of this marked splitting could indicate Jahn–Teller effect [35] due to a degeneration of the ground state of the most symmetrical structure for a d configuration of the As_8 dimer. Since the path of the structural transition $b \rightarrow d$ is rather complicated, we managed to optimize only one saddle point along it, as shown in the energy diagram (Fig. 5). Note that both HF–CC and CNDO/BW calculations give qualitatively close values of energy difference along this transition (Table 1, Fig. 4). It differs sharply from noticeable disagreement between the results of both calculations for cubane-like As_8 structure. Meanwhile, an energy barrier of the transition $b \rightarrow d$ (1.1–1.2 eV) is almost twice higher than in the case of transition $b \rightarrow c$ (Fig. 5). Nevertheless, both c and d configurations of the As_8 cluster are energetically more preferable than the configuration of two separated As_4 tetrahedra (a), thus the process of arsenic dimerization is rather exothermic in both cases.

Different configurations for eight-atom clusters of pnictides (mainly phosphorus) were earlier simulated in several theoretical studies. Semi-empirical MNDO simulation of the dimerization reaction $2P_4 \rightarrow P_8$ gave

an energy preference to a cube-like structure [3], whereas the various ab initio calculations for P_8 clusters [6,8–10] found the energy minimum for two isolated P_4 molecules to be deeper than for the cubic P_8 structure. Main argument in benefit of the latter result showing a smaller probability for cubane configuration was suggested to be a neglect of the repulsion between parallel P–P bonds in the semi-empirical method. In Table 1 we compare results of our calculations with data published by Ballone and Jones [11] for various As_8 clusters. The DFT calculations using the LSD-type exchange and correlation functionals show that As_8 clusters with D_{2h} symmetry possesses practically the same energy as two isolated As_4 molecules, although calculations with the GGA-type functionals make the latter configuration energetically more preferable [11]. Ballone and Jones described an As_8 cluster with C_{2v} symmetry as energetically the most favorable one, but we did not consider it, as mentioned above. Definite differences between results of the HF and DFT calculations are well known [29]. The former usually overestimate bond lengths and underestimate binding energies of the separate chemical bonds and small molecules [36], even when using well-established electron correlation corrections in HF calculations [30–32] this trend does not disappear completely. At the same time, DFT calculations often lead to quite contrary artifacts [37]. From this point of view, we do not dramatize quantitative non-coincidence between the data presented in Table 1, the main idea of this paper being to show qualitative tendencies for the reaction of dimerization $2As_4 \rightarrow As_8$. This is why we have performed such a comprehensive structural optimization for the As_8 cluster model of this reaction using different methods of quantum chemical calculations.

Earlier studies of the photographic process in y-As [19] allowed us to suggest that its sensitivity, comparatively high for a silverless material, could be due to the circumstance that the formation of latent image centers takes place through bond switching between neighboring molecules, which must be an exothermic process. The released energy triggers off a series of further transformations, providing for intensification of the latent image. This agrees with our theoretical calculations arguing in favor of formation of stable As_8 dimers. However, the formation of the first intermediate product (start-up reaction) for

phosphorus is always endothermic, in accord with the kinetic stability of white phosphorus. The least stable phosphorus clusters have been found to be only medium-size ones, P_{12} (D_{3d}) and P_{16} (C_{2h}) [10], but their relative stability with regard to molecular disintegration is lower than that of As_8 clusters with D_{2h} and O_h symmetry, respectively.

In the review paper on y-As [19] a model was proposed, according to which the polymerization proceeds through the formation of stable arsenic clusters, structurally close to the a-As network. Since a characteristic feature of an a-As network is the existence of multi-membered rings, we have chosen a formation of an As_8 dimer as the initial stage of polymerization. This can occur through breaking and switching of bonds between neighboring As_4 molecules. Quantum chemical calculations using modified semi-empirical CNDO/BW code made it possible for the first time to build up a two-dimensional energy surface $\Delta E(z,\theta)$, which is convenient for an analysis of possible paths of structural changes in y-As. The energy barrier of the dimerization reaction was estimated to be 2.6 eV. Two configurations of As_8 clusters have been ascertained as cubane-like one (O_h symmetry), and an eclipsed edge-to-edge structure (D_{2h} symmetry), both being energetically more favorable than two As_4 tetrahedra. In order to verify these results, the ab initio calculations using Hartree–Fock method and incorporating three different electron correlation corrections have been performed for the same model. Ab initio HF–CC calculations qualitatively confirmed the existence of a marked energy barrier for As_8 dimerization (3.2 eV), metastability of the chair-like eight-atom configuration (D_{2d} symmetry), as well as relative stability of the two configurations of As_8 clusters, with D_{2h} and O_h symmetry, respectively. These results can explain rather weak stability of y-As to polymerization observed experimentally under irradiation.

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