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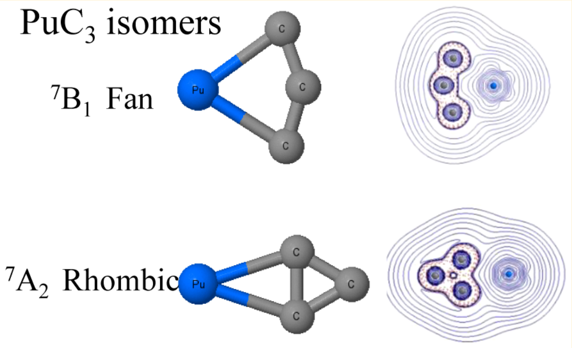
Molecular Structure and Bonding in Plutonium Carbides: A Theoretical Study of PuC_3

Germán Molpeceres,[†] Víctor M. Rayón,[‡] Carmen Barrientos,[‡] and Antonio Largo*,[‡]

[†]Instituto de Estructura de la Materia, IEM-CSIC, Serrano 123, 28006 Madrid, Spain

[‡]Departamento de Química Física y Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, Campus Miguel Delibes, Paseo de Belén 7, 47011 Valladolid, Spain

ABSTRACT: The most relevant species of plutonium tricarbide were characterized using theoretical methods. The global minimum is predicted to be a fan structure where the plutonium atom is bonded to a quasi-linear C_3 unit. A rhombic isomer, shown to be a bicyclic species with transannular C−C bonding, lies about 39 kJ/mol above the fan isomer. A linear PuCCC isomer and a three-membered ring $CPuC_2$ isomer were found to be higher in energy (150 and 195 kJ/mol, respectively, above the predicted global minimum). The possible processes for the formation of these species are discussed, and the IR spectra were predicted to help in possible experimental detection. The nature of the Pu−C interaction has been analyzed in terms of a topological analysis of the electronic density, showing that Pu−C bonding is essentially ionic with a certain degree of covalent character.



■ INTRODUCTION

The study of actinide carbides has received renewed attention in recent years. Their potential use as fuel for new generation nuclear reactors has prompted experimental and theoretical studies. Much of the interest in actinide carbides has focused on their solid-state properties. However, gas-phase properties are also relevant because vaporization is expected at the high temperatures reached in the operation of nuclear reactors.[1] Early mass spectrometry studies[2−5] on uranium, plutonium, and thorium carbides allowed the determination of the relative abundances of different stoichiometric carbides in the gas phase. In addition, thermodynamic properties can be calculated from these data.

More recently, laser evaporation of uranium/carbon alloys combined with matrix isolation IR spectroscopy allowed the observation of different uranium−carbon compounds in the gas phase.[6,7]. It has been shown that UC and linear CUC form in these experiments. In addition, laser ionization of thorium and uranium carbide alloys produced different actinide carbide cluster cations that were detected by Fourier transform ion-cyclotron-resonance mass spectrometry.[8]

Theoretical studies could help in the interpretation of the experiments as well as provide information about the bonding patterns in these types of compounds. To this end, different theoretical studies were carried out to provide information about the molecular structure of small actinide carbides. In particular, uranium carbides have been the subject of recent theoretical studies. Some of these studies were carried out in conjunction with experimental studies,[6−8] whereas other purely theoretical studies on UC_n compounds have also been carried out recently.[9−11] An important conclusion from these studies is that the most stable species is not always observed in the experiments. For example, the linear uranium dicarbide observed in the experiments,[6,7] CUC, is not the lowest-lying isomer of uranium dicarbide. The global minimum is predicted to be a C_{2v}-symmetric (T-shape) $U(C_2)$ isomer, with an energy lying more than 240 kJ/mol lower than that of the linear species.[7,9,10] Recent theoretical studies on uranium dicarbide include the adsorption of the linear and T-shape uranium dicarbide isomers on a graphene surface.[12] Other studies on actinide carbides include a very recent work on NpC, NpC_2, and NpC_4.[13]

On the other hand, little is known about the molecular structure of small plutonium carbides. Datta et al.[5] observed PuC_n^+ ions through radio-frequency spark source mass spectrometry studies, but no structural information is available from these experiments. In a recent study by Pogany et al.,[14] triangular PuC_2 was predicted from theoretical calculations to lie about 381 kJ/mol below CPuC in energy. The molecular structure of PuC_4 has also been theoretically studied in another paper by Pogany et al.,[15] which predicted a fan-type structure as the most stable isomer. To the best of our knowledge, no information is available for other plutonium carbides. In the present work, a theoretical study of the next member in this series is provided. The aim of the present work was to

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characterize the stable isomers of PuC_3 and contribute to the understanding of the growing patterns in plutonium carbides.

■ THEORETICAL METHODS

The theoretical methods employed in the present work are essentially the same as those used in our previous studies on the UC_2 and UC_3 species.[9,11] Preliminary explorations were carried out at the density functional theory (DFT) level, employing the B3LYP exchange-correlation functional.[16,17] Geometry optimizations were then carried out at the coupled-cluster single and double excitation model (CCSD) level. For the carbon atoms, we employed the 6-311+G(3df) basis set;[18] for the plutonium atoms, we employed a combination of the Stuttgart−Dresden effective core potential (ECP60MWB)[19,20] and the [8s7p6d4f] basis set (this combination is referred to as "SDD" in Gaussian 09, and this notation is employed throughout this paper). The Stuttgart−Dresden pseudopotential already includes static relativistic effects. The nature of the stationary points on the potential energy surface was assessed through harmonic vibrational frequency calculations. These calculations provided an estimate of the zero-point energies (ZPE) as well.

Electronic energies have been refined by means of single-point calculations at the CCSD(T) level (CCSD augmented with a noniterative treatment of triple excitations).[21] The T1 diagnostic[22] was used to check the validity of the single-reference approach. In most cases, the T1 values do not suggest a strong multireference character of the wave functions. Nevertheless, we carried out multiconfigurational calculations for the most interesting isomers to check the adequacy of the single-reference theoretical methods. CASSCF[23,24] (complete active space multiconfiguration self-consistent field) optimizations were performed, followed by MRCI[25,26] (multireference configuration interaction) single-point calculations. Multiconfigurational calculations were carried out in conjunction with the MOLPRO implementation of the same basis sets and effective core potentials described above for the single-reference methods. The whole valence space of PuC_3 included the 2s and 2p orbitals of carbon and the 7s, 6d, and 5f orbitals of Pu. This yielded 25 orbitals for PuC_3. A reduced set must be considered for the construction of the active space because the largest feasible number of orbitals is 16. The active space for the fan and rhombic isomers (C_{2v} symmetry point group) was therefore selected, comprising 4 orbitals from representation a_1, 5 from representation b_1, 5 from representation b_2, and 2 from representation a_2 (4552). This space included the 7s, 5f, one 6dπ, and one 6dδ of Pu and six 2p orbitals of the carbons and correlated 12 electrons in 16 orbitals. This selection is usually denoted as CASSCF(12,16). For the MRCI calculations, all configurations with a coefficient larger than 0.02 in the CASSCF wave function were considered. The sums of the squared norms of the selected reference configuration coefficients for the fan and rhombic isomers were 98.90% and 99.24%, respectively. Twenty valence electrons (4 from each C and 8 from Pu) were correlated in the MRCI calculations. Additionally, spin−orbit (SO) coupling was considered using the state-interaction method as implemented in MOLPRO. The SO matrix was diagonalized using spin-free CASSCF wave functions obtained in state-averaged calculations using four roots ($^7A_1$, $^7B_1$, $^7B_2$, and $^7A_2$). All of the single-reference and DFT calculations were carried out with the Gaussian[27] program package, and multireference calculations were carried out with MOLPRO.[28]

The nature of the bonding in plutonium tricarbide isomers was characterized through the topological analysis of the electron density distribution, $\rho(r)$, in the framework of the atoms in molecules theory (AIM).[29] Total electron densities were obtained at the B3LYP level with the same basis sets described above. The bond and atomic properties were calculated using the AIMAll package.[30]

■ RESULTS AND DISCUSSION

A search for possible stable isomers has been carried out on the PuC_3 potential energy surface (PES). While different spin multiplicities were considered for each isomer, we present results only for the lowest-lying state of each isomer. The most relevant isomers are depicted in Figure 1, and their optimized geometries are also given. In Table 1, we report the vibrational frequencies and dipole moments, and their relative energies are given in Table 2.

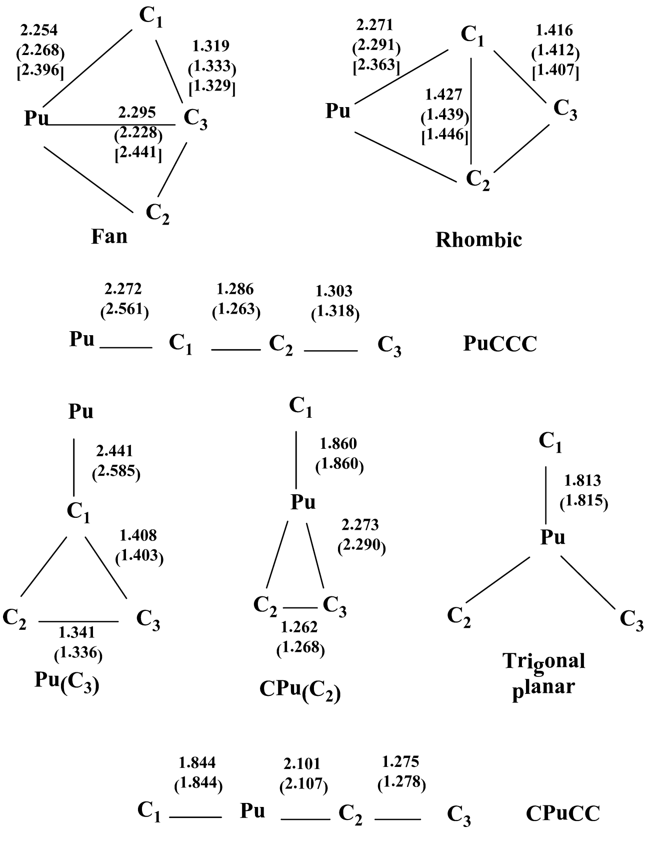

Figure 1. Optimized geometries of the different PuC_3 species at the B3LYP, CCSD (in parentheses), and CASSCF (in squared brackets, when available) levels of theory. Distances are given in Å.

Fan and rhombic isomers were characterized as true minima and result from the lateral addition of a carbon atom to the triangular form of PuC_2 through the Pu−C side and the C−C side, respectively. The fan isomer can also be obtained from a lateral interaction of plutonium with a quasi-linear CCC unit. Both fan and rhombic isomers have septet electronic states ($^7B_1$ and $^7A_2$, respectively). In fact, most of the spin density is localized at the Pu atom (5.50 and 6.04 unpaired electrons localized at Pu, respectively), essentially maintaining the spin multiplicity of the bare atom. This is a variance from the behavior observed for the analogue UC_3 molecule where the lowest-lying isomer, the fan species, has a triplet ground state as

Table 1. Vibrational Frequencies, IR Intensities, and Dipole Moments for the Different PuC_3 Species

species	method	vibrational frequencies (cm^{-1})[a]	μ (D)
fan $^7B_1$	B3LYP/6-311+G(3df)+SDD	322 (b_2,11), 391 (b_1,60), 443 (a_1,67), 709 (a_1,14), 1254 (a_1,5), 1529 (b_2,6)	8.844
	CCSD/6-311+G(3df)+SDD	341 (b_2,11), 391 (b_1,69), 488 (a_1,114), 747 (a_1,11), 1216 (a_1,5), 1477 (b_2,16)	9.741
rhombic $^7A_2$	B3LYP/6-311+G(3df)+SDD	229 (b_1,2), 359 (b_2,25), 408 (a_1,96), 893 (b_2,68), 1053 (a_1,2), 1424 (a_1,1)	9.206
	CCSD/6-311+G(3df)+SDD	238 (b_1,4), 400 (b_2,1), 454 (a_1,104), 1009 (b_2,6), 1125 (a_1,66), 1522 (a_1,4)	8.932
PuCCC $^7\Pi$	B3LYP/6-311+G(3df)+SDD	79/95 (π,0/0),[b] 210 (σ,4), 308/408 (π,17/10),[b] 1228 (σ,9), 1822 (σ,716)	10.226
	CCSD/6-311+G(3df)+SDD	125/140 (π,3/1),[b] 242 (σ,110), 306/422 (π,142/103),[b] 1308 (σ,147), 1915 (σ,1090)	10.257
$Pu(C_3)$ $^5B_1$	B3LYP/6-311+G(3df)+SDD	330 i (b_2), 165 (b_1), 179 (b_2), 227 (a_1), 1221 (a_1), 1590 (a_1)	6.286
	CCSD/6-311+G(3df)+SDD	391 i (b_2), 160 (b_1), 179 (b_2), 230 (a_1), 1305 (a_1), 2018 (a_1)	8.450
$CPU(C_2)$ $^5B_1$	B3LYP/6-311+G(3df)+SDD	44 (b_2,80), 112 (b_1,52), 288 (b_2,9), 492 (a_1,175), 684 (a_1,3), 1827 (a_1,22)	1.884
	CCSD/6-311+G(3df)+SDD	118 (b_2,75), 138 (b_1,56), 329 (b_2,16), 513 (a_1,253), 738 (a_1,10), 1825 (a_1,18)	2.371
CPuCC $^5\Phi$	B3LYP/6-311+G(3df)+SDD	123/121 i (π),[b] 107/109 (π),[b] 465 (σ), 740 (σ), 1844 (σ)	3.889
	CCSD/6-311+G(3df)+SDD	113/115 i (π),[b] 108/130 (π),[b] 478 (σ), 778 (σ), 1852 (σ)	4.348
trigonal planar $^5A_2''$	B3LYP/6-311+G(3df)+SDD	84 i (e'), 192 (a_2'',38), 807 (a_1',0), 815 (e',61)	0.000
	CCSD/6-311+G(3df)+SDD	141 (e',21), 245 (a_2'',27), 796 (a_1',0), 876 (e',18)	0.000

[a] Mode symmetry and IR intensity (km/mol) are in parentheses. [b] Nondegenerate π vibrational frequencies are due to the Renner–Teller effect.

Table 2. Relative Energies (kJ/mol) at Selected Levels of Theory for the Most Relevant PuC_3 Species with ZPE Corrections Included

	fan $^7B_1$	rhombic $^7A_2$	PuCCC $^7\Pi$	$Pu(C_3)$ $^5B_1$	$CPU(C_2)$ $^5B_1$	CPuCC $^5\Phi$	trigonal planar $^5A_2''$
B3LYP/6-311+G(d)+SDD	0.0	18.4	64.9	119.7	211.4	268.8	772.1
CCSD/6-311+G(d)+SDD	0.0	23.5	123.3	170.5	202.6	271.0	792.0
CCSD(T)/6-311+G(d)+SDD	0.0	38.9	150.1	199.1	195.1	267.7	709.6
CASSCF (12,16)	0.0 (0.954)[a]	33.9 (0.962)[a]					
MRCI	0.0	45.0					
ΔSO[b]	0.0	9.7					

[a] Weight of the leading configuration in the CAS wave function. [b] Contribution of the spin–orbit coupling (SOC) to the relative energies. The SOC is 35.7 and 26.0 kJ/mol for the fan and rhombic isomers, respectively.

opposed to the quintet ground state of the U atom. Nevertheless, in both isomers of PuC_3, low-lying quintet states were found. In the case of the fan isomer, a $^5A_1$ state was found to lie just around 5 kJ/mol above the $^7B_1$ state in energy at the CCSD(T) level of theory. For the rhombic isomer, the lowest-lying quintet state ($^5B_1$) lies around 24 kJ/mol at the same level of theory. Even though these energy differences are small, all theoretical levels employed in the present work point to the septet states as the lowest-lying states in both cases. Therefore, we have adopted the septet states in the following discussion. Through the interaction of triangular PuC_2 with a carbon atom, another species can be obtained. If the carbon atom is attached to the plutonium atom, a three-membered ring isomer is formed. This is denoted as $CPU(C_2)$ to indicate that Pu is bonded to an exocyclic carbon atom and a C_2 unit. The $CPU(C_2)$ species is also a true minimum on the PES because it has all real frequencies, but its lowest-lying state is a quintet ($^5B_1$).

There is another three-membered ring isomer, denoted as $Pu(C_3)$, with the plutonium atom in an exocyclic position that results from a side interaction with the carbon atom of PuC with a C_2 unit. However, the lowest-lying state of this isomer ($^5B_1$) has an imaginary frequency at both the B3LYP and CCSD levels, suggesting that this species is not a true minimum. The imaginary frequency corresponds to the degenerate rearrangement of the rhombic isomer (displacement of the plutonium atom from an apex to a side of a cyclic C_3 unit). In fact, following the associated normal mode, the rhombic isomer was finally reached.

Two different linear species were characterized, one with the plutonium atom in a terminal position and the second with the plutonium atom within the chain. PuCCC has a $^7\Pi$ electronic state and was found to be a true minimum. This isomer is formed upon the interaction of plutonium with a terminal carbon atom of linear CCC. The second linear species, CPuCC, has a lowest-lying quintet electronic state ($^5\Phi$). Nevertheless, this species has two imaginary frequencies (corresponding to π vibrational normal modes) at both the B3LYP and CCSD levels and therefore cannot be considered a true minimum. Following the normal mode associated with the imaginary frequency and performance of an optimization in C_s symmetry, the $CPU(C_2)$ isomer was finally reached. CPuCC is formed either from the interaction of linear CPuC with a carbon atom or from the interaction of C_2 with PuC.

Finally, a trigonal planar species was characterized with a quintet electronic state, although the singlet state is also very close in energy. At the B3LYP level, this species has two degenerate (e') imaginary frequencies. However, at the CCSD level, all of its frequencies are real, showing that it is a true minimum on the PES at this level of theory. The trigonal planar isomer results from the interaction of a carbon atom with the plutonium atom of the linear CPuC species.

The fan isomer has C–C bond distances close to those of typical double bonds and somewhat longer than those found in linear C_3.[31] The CCC bond angle also deviates considerably from linearity with a value around 143°. These geometrical parameters suggest that, upon interaction with the plutonium atom, the linear C_3 chain is considerably modified. Another interesting point is that the distance between plutonium and the central carbon of the C_3 unit does not rule out a bonding interaction because it takes a value close to those found for the two equivalent terminal atoms. In the case of the rhombic

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isomer, the Pu−C distances are very similar to those found for the fan isomer, whereas the C−C distances are much longer. It is also worth noting that the transannular C−C distance in the rhombic isomer is very similar to the peripheral distances. These values suggest that this isomer quite likely has true transannular C−C bonding and therefore could be classified as a bicyclic species.

The linear PuCCC isomer also shows a Pu−C bond distance close to 2.3 Å at the B3LYP level, although a slightly longer value was found using the CCSD method. On the other hand, the C_1−C_2 bond distance at CCSD level is slightly shorter than that at the B3LYP level. A similar effect is observed in the Pu(C_3) species, although with smaller changes from B3LYP to CCSD. The C−C bond distances in the linear PuCCC isomer, especially the bond closest to the Pu atom, are very similar to those found in linear C_3.[31] The longest Pu−C distance was found for the Pu(C_3) species with a value of 2.585 Å at the CCSD level, suggesting a weak Pu−C bond. As we have mentioned before, this species is not a true minimum and evolves toward the rhombic isomer.

In the linear CPuCC and the isomers of the three-membered ring CPU(C_2), two different types of Pu−C bonds are found. When Pu is bonded to a carbon atom that is also bonded to a carbon atom, the Pu−C distance is similar to that found in the fan, rhombic, and PuCCC isomers with values around 2.1−2.3 Å. For Pu−C bonds where the carbon atom is bonded to only plutonium, a much shorter distance of around 1.84−1.86 Å is found. This reflects the trend to form multiple bonds in the latter case. For the trigonal planar species where all carbon atoms are bonded only to Pu, the bond distances are particularly short (1.815 Å).

The calculated dipole moments for the plutonium tricarbide species suggest a high ionic character for the Pu−C bonds. The trigonal planar isomer has a zero dipole moment by symmetry, and for the CPU(C_2) and CPuCC species, the dipole moment is moderate due to the plutonium atom occupying a central position. However, all species with the plutonium atom in a terminal position, particularly the fan, rhombic, and linear PuCCC isomers, have large dipole moments in the range of 9−10 D. The character of the Pu−C bonds is addressed later with the help of an electron density analysis.

The relative energies for all studied PuC_3 species at the B3LYP, CCSD, and CCSD(T) levels of theory are given in Table 2. Essentially, the three levels of theory employed agree with the stability order, with the only exception being the reversed order between Pu(C_3) and CPU(C_2) at the CCSD(T) level. At this level of theory, which is usually the most reliable, the latter is placed slightly below the former. The relative energy order according to the CCSD(T) values, starting from the most stable species, is as follows:

$$\text{fan} < \text{rhombic} < \text{PuCCC} < \text{CPu}(C_2) < \text{Pu}(C_3) < \text{CPuCC} < \text{trigonal planar}$$

The most interesting result from our theoretical calculations is that the fan isomer is predicted to be the global minimum for the PuC_3 system. Only the rhombic isomer is close enough to be a possible alternative. The rest of the species are predicted to lie in energy well above 100 kJ/mol higher than that of the fan isomer, at least at the CCSD(T) level. It is interesting to point out that the three most stable species have high-spin states (septet), and the inclusion of higher-order correlation effects does not seem to favor quintet states over septet states.

Given the relatively low energy gap between the fan and rhombic isomers, we carried out multiconfigurational calculations to analyze the main factors contributing to their relative stability. As can be seen in Table 2, both isomers have weights of the leading configurations well above 0.9, suggesting that multireference effects should not be very important. At the CASSCF level, the rhombic isomer lies 33.9 kJ/mol above the fan species in energy. At the MRCI level, this relative energy difference is 45.0 kJ/mol, which is close to the CCSD(T) value of 38.9 kJ/mol. The spin−orbit coupling (SOC) for the fan and rhombic isomers was computed (see Table 2), and this correction shows an incremental energy difference between them of 9.7 kJ/mol. We can therefore conclude that both single-reference and multireference methods agree with the prediction that the fan species is the most stable isomer of PuC_3.

The preference for fan and rhombic species over three-membered rings and linear isomers is consistent with previous studies on small carbides. In the case of UC_3, a similar behavior was observed:[11] the fan isomer was also predicted as the global minimum. In addition, a systematic study of third row main group tricarbides[32] has shown that fan or rhombic isomers are favored for less electronegative elements, whereas for more electronegative elements, three-membered rings or linear species are preferred. Uranium and plutonium, both having low electronegativities, behave like electropositive atoms such as K or Ca rather than like electronegative atoms such as Se or Br.

It seems that the stability of the PuC_3 species is dictated by two different factors: the arrangement of the C_3 unit and the interaction of the plutonium atom with the carbon unit. First, the preference for the fan isomer over the rhombic species, as well as the stability of linear PuCCC being higher than that of cyclic Pu(C_3), is mainly a consequence of linear CCC being more stable than cyclic C_3. Second, the lateral interaction of plutonium with the C_3 unit is favored over the interaction of plutonium with a single carbon atom. Thus, the fan isomer, where Pu interacts laterally with a quasi-linear CCC chain, is more stable than linear PuCCC, where the interaction of Pu with the carbon chain takes place through a single carbon atom. In a similar way, the rhombic isomer, which results from the side interaction of plutonium with a triangular C_3 unit, is more stable than cyclic Pu(C_3), where Pu interacts through an apex of the triangular C_3 moiety. This is mainly related to the electropositive nature of the plutonium atom which should give rise to mainly ionic plutonium−carbon interactions. The less stable species are those where the C_3 unit is fragmented, either partially (CPU(C_2) or linear CPuCC) or completely (trigonal planar species). In these species, the C−C bonds are partially or completely substituted by Pu−C bonds, resulting in less stable structures. Further, the Pu−C bonds are slightly stronger, possibly as a consequence of a certain covalent character giving rise to shorter Pu−C bond distances.

The following discussion on the preferential PuC_3 isomer that could be produced depending on the formation process is based solely on thermodynamic arguments. Therefore, we discuss the thermodynamically preferred product in each case. We identified four different types of formation processes:

(1) Interaction of plutonium atoms with C_3. Because C_3 has a linear ground state,[31] this interaction could lead to the fan isomer (lateral interaction) or the linear PuCCC isomer if the plutonium atom is bonded to a terminal carbon atom. Given the higher stability of the former isomer, it is expected that only

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the fan isomer could be formed through this process. The enthalpy associated with the formation of the fan isomer from Pu + C_3 is about 409 kJ/mol at the CCSD(T) level (for the production of the rest of the possible isomers, the corresponding enthalpy can be deduced from the relative energies shown in Table 2). This value suggests that the PuC_3 fan isomer has a relatively large stability toward dissociation.

(2) Addition of plutonium monocarbide to C_2. This process may generate linear PuCCC (interaction through the carbon atom), linear CPuCC (interaction through the plutonium atom), cyclic Pu(C_3) (side interaction through the carbon atom), or CPU(C_2) (side interaction through the plutonium atom). Given the relative stabilities, the most favored product should be linear PuCCC. The reaction enthalpy for PuCCC formation at the CCSD(T) level of theory is about 628 kJ/mol.

(3) Addition of a carbon atom to plutonium dicarbide. According to Pogany et al.,[14] triangular PuC_2 is predicted to be more stable than linear CPuC (by about 381 kJ/mol). If a carbon atom interacts with triangular PuC_2, fan, rhombic, or CPU(C_2) isomers could be produced. Therefore, the most stable one, the fan isomer, should be generated according to thermodynamic arguments. However, because the carbon atom could be attracted by the positive charge at Pu, it could be argued that CPU(C_2) should be the preferentially formed isomer. On the other hand, if we begin with the less stable CPuC linear isomer interacting with a carbon atom, trigonal planar, linear CPuCC, or CPU(C_2) species can in principle be obtained. In this case, CPU(C_2) should be the preferred product. The formation of CPU(C_2) from C + CPuC is exothermic by 725 kJ/mol, whereas the reaction of C atoms with PuC_2 to produce the PuC_3 fan isomer has a reaction enthalpy of 515 kJ/mol (both values obtained at the CCSD(T) level).

The predicted IR spectra for the four possible products of the previously discussed processes (fan, rhombic, PuCCC, and $CPuC_2$) are schematically depicted in Figure 2. The intensities of the different bands are given in relative units with the most intense line as a reference. Even though the fan, rhombic, and $CPuC_2$ isomers have the most intense lines (near 500 cm^{-1}), corresponding in all cases to the Pu−C_n (n being either 2 or 3) stretching, it should be possible to distinguish their IR spectra by their second most intense lines, which should appear at very different frequencies in each case. The linear PuCCC isomer has a predicted IR spectrum that is very different from the rest of the possible isomers, with the most intense line near 1900 cm^{-1} (corresponding to C−C stretching).

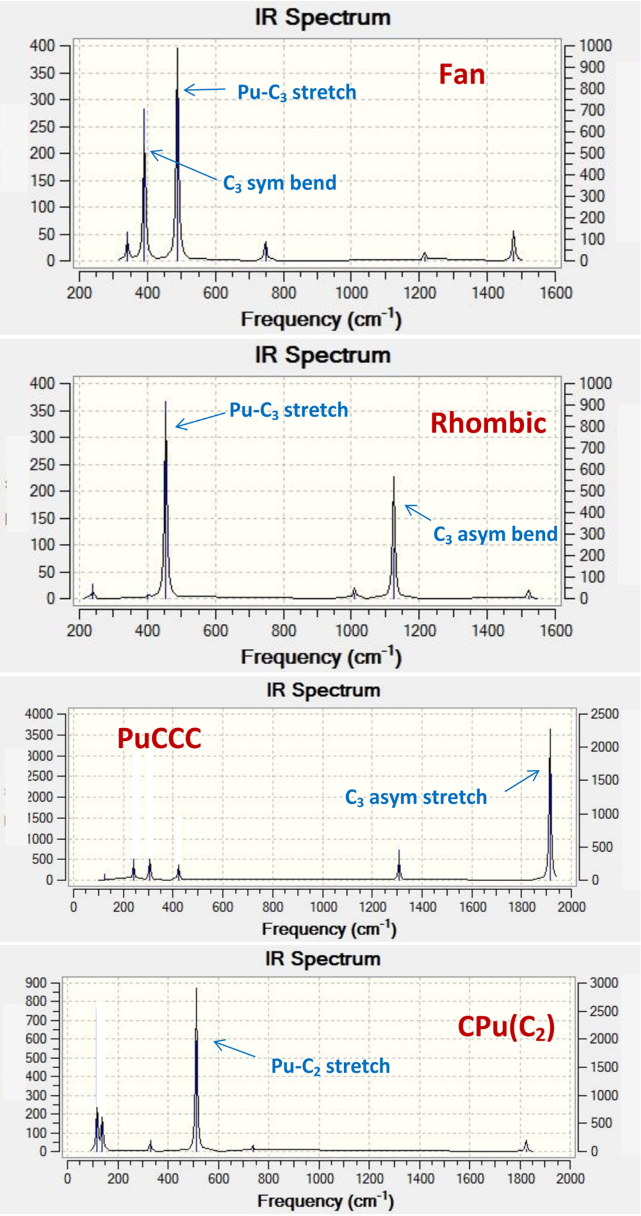

Figure 2. Schematic representation of the IR spectra of the most relevant PuC_3 isomers.

The nature of the bonding in the different plutonium tricarbide species was characterized with the application of the topological analysis of the electronic charge density.[29] This analysis allowed the identification of critical points in the one-electron density $\rho(r)$ and therefore provided information about the real connectivity in a particular species. In the case of plutonium tricarbide, only bond critical points and ring critical points are relevant. In addition, analyses of the Laplacian of the electronic density and other magnitudes computed at bond critical points, such as the total energy density $H(r)$, potential energy density ($V(r)$), and kinetic energy density ($G(r)$), give information about the nature of the interaction between atoms.[33,34] The molecular graphs of the electron density for the nonlinear PuC_3 species are shown in Figure 3. Molecular graphs for the linear species are not shown because these structures have only bond critical points between adjacent atoms. The contour maps of the Laplacian of the electron density for all PuC_3 species are given in Figure 4.

The molecular graph for the fan isomer shows two peripheral Pu−C bond critical points, but no bond critical point between plutonium and the central carbon atom of the C_3 unit was found. Therefore, only one ring critical point was characterized, and the fan isomer can be classified as a monocyclic species. On the other hand, the rhombic isomer has a different molecular graph. In addition to two Pu−C and two C−C peripheral bonds, a transannular C−C bond was also found, a fact consistent with the relatively short C_1−C_2 distance observed at all levels of theory. Therefore, two ring critical points were characterized, and the rhombic isomer can be classified as a bicyclic species.

For the Pu(C_3) species, the molecular graph clearly shows a three-membered ring formed by the C_3 unit, as three C−C bond critical points and a ring critical point were found. Therefore, this species can be described as a cyclic structure

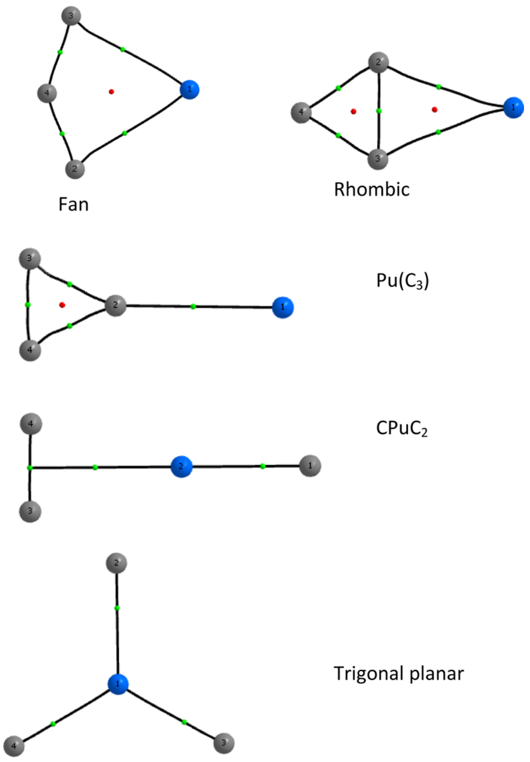

Figure 3. Molecular graphs of the electron density for the different PuC_3 species. Small green spheres are bond critical points, and small red spheres are ring critical points.

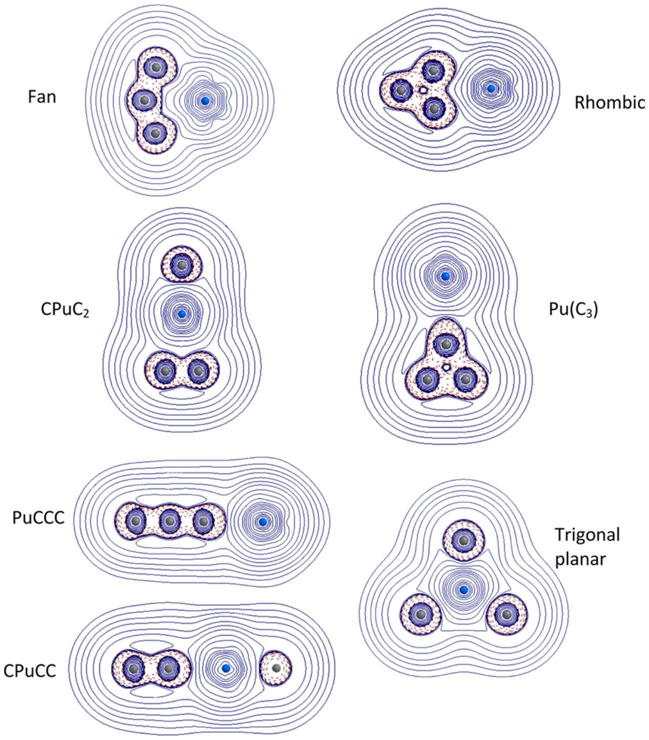

Figure 4. Contour maps of the Laplacian distribution of the electron density for the different PuC_3 species. Red dashed lines indicate regions of electronic charge concentration ($\nabla^2\rho(r) < 0$), and blue continuous lines denote regions of electronic charge depletion ($\nabla^2\rho(r) > 0$).

with an exocyclic plutonium atom. On the other hand, the $CPU(C_2)$ isomer does not show any ring critical point. Only one C−C bond critical point and two Pu−C bond critical points were found. Therefore, this isomer can be described as a PuC unit π-bonded to the C_2 moiety through the plutonium atom, similar to a T-shape structure. In the case of the trigonal species, only three Pu−C bond critical points were found.

An inspection of the contour maps of the Laplacian of the electron density for the different PuC_3 species (Figure 4) suggests that all Pu−C bonds should correspond to closed-shell interactions,[33] whereas all C−C bonds should correspond to typical shared interactions.[33] This global view was confirmed by the topological properties of the electronic densities collected in Table 3. C−C bond critical points are characterized by large values of $\rho(r)$ and negative values of its Laplacian $\nabla^2\rho(r)$, which are typical characteristics of shared interactions.[33] Their large values for the total energy density $H(r)$ confirm the essentially covalent nature of these interactions.[34] Another property which may help in analyzing the covalent character of an interaction is the relationship between $V(r)$ and $G(r)$. Values of $V(r)/G(r)$ greater than 2 are typical of covalent interactions, whereas noncovalent interactions usually show values smaller than 1. Values between 1 and 2 suggest partially covalent bonds. There is no doubt that all C−C bonds, including the transannular C−C bonding in the rhombic isomer, show clear characteristics of covalent bonds with values for $V(r)/G(r)$ greater than 2.

Pu−C bonds have relatively small values of $\rho(r)$ and positive values of $\nabla^2\rho(r)$, thus confirming that Pu−C bonds can be classified as closed-shell interactions. In most cases, Pu−C bonds have a small degree of covalent character, as suggested by the negative value (but small in absolute value) of $H(r)$ and the value of the relationship $V(r)/G(r)$ between 1 and 2. Therefore, the Pu−C interactions in the PuC_3 species can be classified as closed-shell with a small degree of covalent character. Nevertheless, the Pu−C bonds with small bond distances show higher covalent character. This is evident in the cases of the $CPU(C_2)$ and linear CPuCC species, where two different Pu−C bond distances are found (see Figure 1). The shortest Pu−C bond in each case is characterized by a negative value of $H(r)$ (−0.1603 and −0.1776 au, respectively), much higher in absolute value than those values corresponding to the longest bond distance (−0.0379 and −0.0804 au, respectively). The trigonal planar isomer, having the shortest Pu−C bond distance of all the PuC_3 species, has Pu−C bonds with the smallest value of $\nabla^2\rho(r)$, the most negative value of $H(r)$, and a $V(r)/G(r)$ relationship very close to 2, therefore showing the highest covalent character for Pu−C bonds.

The predominant ionic (closed-shell) character of Pu−C bonds was also confirmed by the AIM atomic charges shown in Table 4. For those species with Pu bonded to just one carbon atom, namely PuCCC and $Pu(C_3)$, the charge on the plutonium atom is close to 1. This charge is noticeably higher for those isomers where Pu is bonded to two or more carbon atoms.

Therefore, we conclude that Pu−C bonds can be classified as closed-shell interactions mainly of ionic character with a certain degree of covalent character. The covalent character varies for the different PuC_3 species. In general, it is found that the shorter the Pu−C distance, the larger the degree of covalent character. These conclusions generally agree with the preceding discussion on the relative stability of PuC_3 species.

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Table 3. Local Topological Properties (in au) of the Electron Density Distribution Calculated at the Position of the Bond Critical Points for the Different PuC_3 Species[a]

isomer	bond	$\rho(r)$	$\nabla^2\rho(r)$	$\lvert V(r)\rvert/\lvert G(r)\rvert$	$H(r)$
fan $^7B_1$	$Pu-C_1$, $Pu-C_2$	0.1144	0.1365	1.5819	−0.0475
	C_1-C_3, C_3-C_2	0.3408	−0.9137	3.3512	−0.3975
rhombic $^7A_2$	$Pu-C_1$, $Pu-C_2$	0.0999	0.2187	1.3866	−0.0346
	C_1-C_2	0.2692	−0.3639	2.5752	−0.2491
	C_1-C_3, C_2-C_4	0.2788	−0.4889	2.8587	−0.2645
PuCCC $^7\Pi$	$Pu-C_1$	0.1389	0.2185	1.5337	−0.0081
	C_1-C_2	0.3559	−0.1094	3.8309	−0.4229
	C_2-C_3	0.3863	−0.1299	4.5181	−0.4537
$Pu(C_3)$ $^5B_1$	$Pu-C_1$	0.0822	0.1156	1.4639	−0.0251
	C_1-C_2, C_1-C_3	0.2777	−0.3299	2.4585	−0.2624
	C_2-C_3	0.3435	−0.8727	3.2794	−0.3887
$CPU(C_2)$ $^5B_1$	$Pu-C_1$	0.1989	0.1523	1.8081	−0.1603
	Pu−CC	0.1058	0.1909	1.4428	−0.0379
	C_2-C_3	0.3963	−1.2249	3.4502	−0.5174
CPuCC $^5\Phi$	$Pu-C_1$	0.2097	0.1309	1.8445	−0.1776
	$Pu-C_2$	0.1511	0.1056	1.7528	−0.0804
	C_2-C_3	0.3861	−1.2354	3.7368	−0.4867
trigonal planar $^5A_2''$	$Pu-C_1$, $Pu-C_2$, $Pu-C_3$	0.2382	0.0276	1.9706	−0.2283

[a] The electronic charge density [$\rho(r)$], the Laplacian [$\nabla^2\rho(r)$], the relationship between the local kinetic energy density [$G(r)$] and the local potential energy density [$V(r)$], and the total energy density [$H(r)$].

Table 4. Net Atomic Charges, $q(\Omega)$, Obtained by Integrating the Charge Density over the Atomic Basin (in au)

Ω	fan $^7B_1$	rhombic $^7A_2$	PuCCC $^7\Pi$	$Pu(C_3)$ $^5B_1$	$CPU(C_2)$ $^5B_1$	CPuCC $^5\Phi$	trigonal planar $^5A_2''$
Pu	+1.39	+1.16	+1.07	+0.71	1.65	+1.63	+1.15
C_1	−0.43	−0.55	−0.14	−0.43	−0.59	−0.62	−0.38
C_2	−0.43	−0.55	−0.35	−0.14	−0.53	−0.87	−0.38
C_3	−0.53	−0.06	−0.42	−0.14	−0.53	−0.14	−0.38

■ CONCLUSIONS

The most relevant isomers of plutonium tricarbide were characterized through theoretical methods. The global minimum is predicted to be a fan structure, where the plutonium atom is bonded to a quasi-linear C_3 unit. A rhombic isomer, shown to be a bicyclic species with transannular C−C bonding, lies only about 39 kJ/mol higher in energy. Other species, such as the linear PuCCC isomer and the three-membered ring $CPuC_2$ isomer, lie much higher in energy (150 and 195 kJ/mol, respectively, above the fan isomer). The relative stabilities of PuC_3 species have been rationalized in terms of the carbon unit structure and the nature of its interaction with plutonium. The higher stability of the fan isomer compared to that of the rhombic species, as well as the higher stability of linear PuCCC compared to that of cyclic $Pu(C_3)$, is mainly a consequence of the higher stability of linear CCC compared to that of cyclic C_3. Furthermore, the lateral interaction of plutonium with the C_3 unit is favored over the interaction of plutonium with a single carbon atom.

The preference for the formation of the different PuC_3 isomers has been discussed in terms of thermodynamic arguments taking into account the possible production processes: interaction of plutonium atoms with C_3, addition of a carbon atom to a PuC_2 unit, or interaction of PuC with C_2. It is then possible that different PuC_3 species could be produced depending on the experimental conditions. Predictions of the IR spectra for the main isomers have been provided to assist in their possible experimental detection.

Finally, an analysis of the bonding in the different PuC_3 isomers has been carried out by applying a topological analysis of the electronic charge density. It has been shown that the Pu−C interactions are mainly ionic, since they correspond to closed-shell interactions. Nevertheless, a partial covalent character is observed in all cases and particularly in those species where plutonium is bonded to a single carbon atom.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: alargo@qf.uva.es.

Notes

The authors declare no competing financial interest.

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