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# Computational Assessment of an Elusive Aromatic N$_3$P$_3$ Molecule

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S Supporting Information

ABSTRACT: We computationally proved that the planar aromatic hexagonal isomer N$_3$P$_3$ with the alteration of N and P is the second most stable structure for the N$_3$P$_3$ stoichiometry. We found that the aromatic isomer has high barriers for transition into the global minimum structure or into the three isolated NP molecules, making this structure kinetically stable. We showed that the sandwich N$_3$P$_3$CrN$_3$P$_3$ molecule corresponds to a minimum on the potential energy surface; thus, the aromatic N$_3$P$_3$ molecule has a potential to be a new ligand in chemistry.
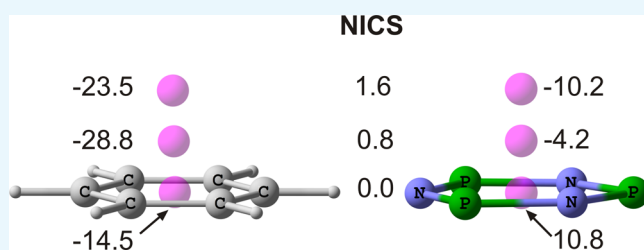
1. INTRODUCTION

Hexaazabenzene N$_6$ and hexaphosphabenzene P$_6$ are valence isoelectronic analogues of benzene, and therefore, one may think that they should have a planar hexagonal structure due to aromaticity. However, both of these species have turned out to be unstable at the D_{6h} planar structures. A significant amount of theoretical work was dedicated to assess the stability and aromaticity of planar hexagonal N$_6$ as a potential 6π-aromatic system.[1] According to the most accurate calculations of the geometry and frequencies of the planar hexagon structure performed by Roos and co-workers[2] and Tobita and Bartlett[3] at the CASPT2/BS2 and CCSD(T)/cc-pVTZ levels of theory, respectively, the D_{6h} form of N$_6$ was found to be a second-order saddle point. Geometry optimization along imaginary modes leads to a slightly distorted D_2 cyclic structure 0.25 kcal mol^{-1} (CASPT2/BS2)[2] lower in energy than the D_{6h} structure. Moreover, it dissociates without any barrier into three N$_2$ molecules. Roos and co-workers concluded that the planar cyclic form of N$_6$ is not stable. Tobita and Bartlett[3] found that the D_2 structure is a local minimum with a low vibration frequency (73.6 cm^{-1}) leading to dissociation and also concluded that the structure may easily dissociate into three N$_2$ units.[3] Therefore, the benzene-like form of N$_6$ is unlikely to exist.

It is a different story for the P$_6$ molecule. In 1985, Scherer et al.[4] obtained a triple-decker sandwich complex {(μ^5-Me$_5$C$_5$)-Mo}$_2$(μ,η^6-P$_6$) containing a planar P$_6$ ring with equal P−P bond lengths. However, theoretical calculations showed that at least 10 nonplanar P$_6$ isomers (Figure 1) were lower in energy than the planar benzene-like D_{6h} structure.[5−15]

According to the most accurate calculations by Hiberty and Volatron[14] and by Galeev and Boldyrev,[15] the global minimum of P$_6$ is the benzvalene-like structure **I.1**. The prismane-like
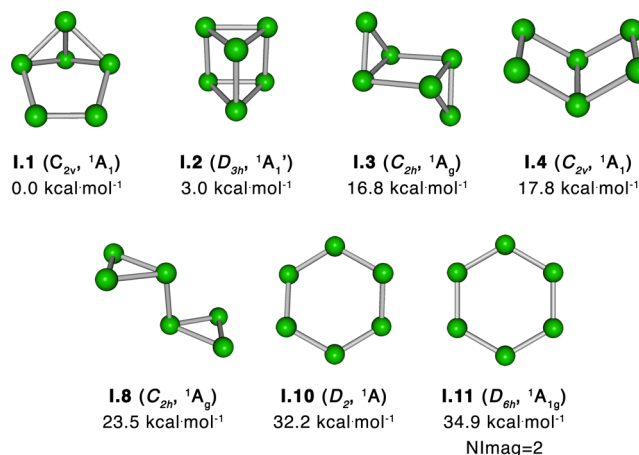

Figure 1. Representative optimized structures of P$_6$, their point group symmetries, spectroscopic states, and zero-point energy (ZPE)-corrected (B3LYP/6-311+G*) relative energies. Reproduced from ref 15.

isomer **I.2** is the second lowest one, and the other isomers lie significantly higher in energy. Moreover, the D_{6h} structure **I.11** is not even a local minimum but a second-order saddle point. Geometry optimization along the imaginary modes leads to the distorted structure **I.10** (D_2, ^{1}A). The rearrangement of **I.11** into **I.10** along the e$_{2u}$ doubly degenerate frequency mode occurs because of the pseudo Jahn−Teller effect resulting from vibronic coupling of highest occupied molecular orbital
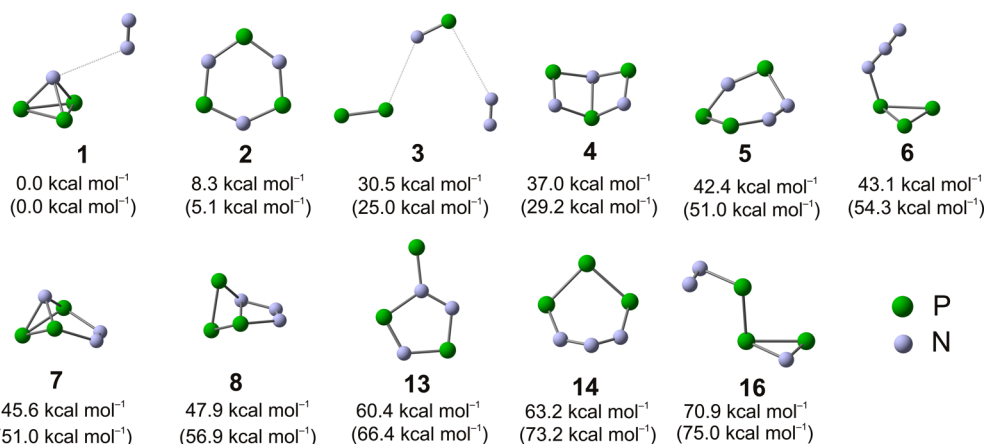
Figure 2. Representative optimized structures and relative energies of the lowest isomers of N_3P_3 (PBE0/6-311+G*+ZPE). The order of the isomers is given according to relative energies at PBE0/6-311+G*. Data on calculations performed by using CCSD(T)/aug-cc-pvQZ//PBE0/6-311+G* are shown in brackets. In this figure and in Figures 3−5, phosphorus atoms are green and nitrogen atoms are lilac. A more complete list of isomers and their description are given in the Supporting Information (Figure S1).
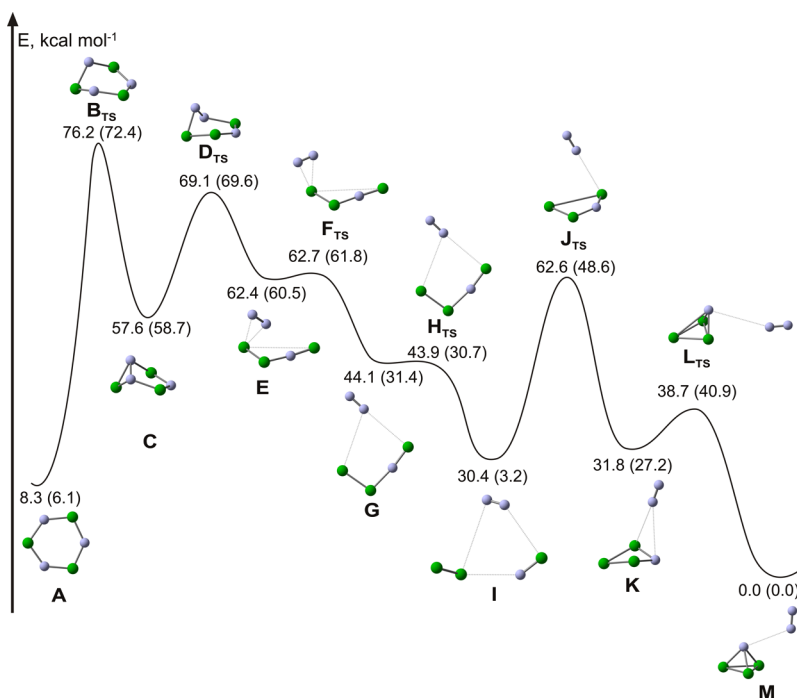

Figure 3. The mechanism of intramolecular rearrangements of hexagon-like structure **2** (**A**) into the most thermodynamically stable structure **1** (**M**), according to the DFT PBE0/6-311+G*+ZPE calculations. Data on single-point calculations performed by using CCSD(T)/6-311+G(d) are shown in brackets. Here and in Figure 4, all energy values are estimated with respect to structure **1** (**M**).

(HOMO) − 1 (e_{2g}) and lowest unoccupied molecular orbital (LUMO) (e_{2u}).[15]

On the basis of these data, one may think that the mixed aromatic N_xP_{6-x} ($x = 1−5$) molecules would hardly be stable. However, a recent synthesis of the mixed $P_2N_3^-$ cyclic aromatic anion in a solid state by Velian and Cummins[16] gives us hope that some of the mixed N_xP_{6-x} molecules could be viable. Probably the most surprising fact is that the $N_3P_3X_6$ derivatives of the N_3P_3 molecule are well-known in chemistry.[17−28] Yet, the isolated N_3P_3 molecule is very elusive. There are three publications on the structure and aromaticity of the 1,3,5-triphosphazatriene.[29−31] The authors of the first two articles focused on the planar 1,3,5-triphosphazatriene isomer, and they concluded that this molecule is planar and aromatic. There is

also a joint experimental and theoretical work[31] on 1,3,5-triphosphazatriene, in which an observation of this molecule under the matrix isolation conditions is reported, but the relative stability of this isomer with respect to alternative structures was not studied. In this work, we explored the isomerism of the N_3P_3 stoichiometry and evaluated the viability of the N_3P_3 aromatic molecule as a potential new ligand in inorganic chemistry.

2. RESULTS AND DISCUSSION

2.1. Stability of the Aromatic N_3P_3 Molecule. The lowest isomers of N_3P_3 are shown in Figure 2. According to our PBE0/3-21G initial global minimum search using the Coalescence-Kick method, the high symmetry D_{3h} singlet
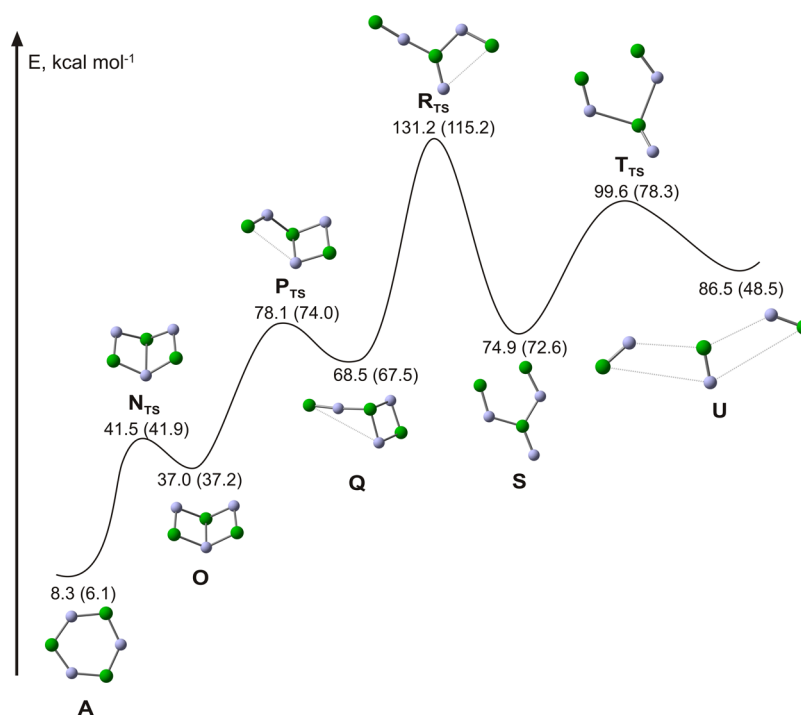
Figure 4. Mechanism of dissociation of hexagon-like structure **2** (**A**) into three PN molecules, according to the PBE0/6-311+G*+ZPE calculations. Data on single-point calculations performed by using CCSD(T)/6-311+G(d) are shown in brackets.

structure is the global minimum. The complex of NP_3 distorted tetrahedron and N_2 molecule connected to each other by van der Waals forces is the second most stable isomer. However, when we reoptimized the lowest energy structures at the PBE0/6-311+G* level of theory, we found that the van der Waals complex **1** is a global minimum and the planar hexagon-like structure **2** is the second most stable isomer. At the highest level of theory (CCSD(T)/aug-cc-pvQZ//PBE0/6-311+G*+ZPE/PBE0/6-311+G* here and elsewhere) isomer **1** is more stable than **2** by about 5.1 kcal mol^{-1}. The third isomer of the N_3P_3 stoichiometry is a van der Waals complex **3** between three diatomic molecules N_2, NP, and P_2, lying about 25.0 kcal mol^{-1} higher in energy. We found many local minima (LMs) similar to the structures **1** and **3**, which differ from them by orientation of weakly bound molecules. The high symmetry hexagon-like structure **2** is thermodynamically stable toward dissociation into three diatomic molecules, but it is unstable toward dissociation into NP_3 + N_2 complex. Other isomers were found to be significantly higher in energy (see Supporting Information). Planar hexagonal-like structures of two CHP_5 and $C_2H_2P_4$ molecules were previously shown[15] to be the minima at two density functional theory (DFT) methods (B3LYP/6-31G** and B3LYP/6-311++G**), but to be the second order saddle points at the CCSD(T)/6-311++G** level of theory. Therefore we re-optimized geometry of the hexagonal structure of N_3P_3 at CCSD(T)/6-311+G* level of theory We found that isomer **2** is a minimum at this level of theory. Thus, we do not observe method dependence for planarity of N_3P_3.

Because of the thermodynamic instability of structure **2**, we performed the search for the transition state (TS) between structures **1** and **2**. The computationally found potential energy surface profile is schematically shown in Figure 3. According to the calculations (DFT PBE0/6-311+G*+ZPE), on the first stage of the reaction, the distortion of hexagon-like structure **2**

(named **A** in Figure 3) occurs, which is caused by removing two nitrogen atoms from the plane of the molecule. This process occurs via the TS B_{TS} with the barrier of about 70 kcal mol^{-1}. It is accompanied by transition of the system into the local minimum **C**, which is less stable than structure **A** by more than 50 kcal mol^{-1}. Then, one of the above discussed nitrogen atoms jumps over the adjacent phosphor atom (TS D_{TS}), which leads to the formation of a weakly bound complex of P_3N plane and N_2 molecule (structure **E**). Its dissociation via the TS F_{TS} leads to the kinetically unstable van der Waals complex **G**, in which virtually barrier-free (H_{TS}) relaxes into stable planar structure **3** (named **I** in Figure 3), representing the van der Waals complex between three diatomic molecules N_2, NP, and P_2. The subsequent approaching of P_2 and PN molecules leads to the TS J_{TS}, and the gradient descent along the transition vector converts the reaction system into isomer **K**. In structure **K**, bond lengths of the tetra-atomic fragment are equal to 2.153 Å (P−P) and 1.675 Å (P−N) (see Figure S2). This process requires overcoming the energy barrier of 30 kcal mol^{-1}. The final stage of the transition under study is associated with the stabilization of the nitrogen atom in the vertex of NP_3 pyramid. Transformation of structure **K** into global minimum **M** (structure **1**) occurs via TS L_{TS}, which was found to be a singlet biradical. Because the TS is an open-shell system, we performed single-point calculations of the found isomers using the CAS(18,12)/6-311+G* method. These calculations confirm that TSs L_{TS} and J_{TS} are open-shell systems (the leading coefficient = 0.76). All other structures localized by the DFT method were found to be good one-electron configuration ones (the leading coefficient > 0.90). Thus, the transition from structure **2** into the most thermodynamically stable structure **1** as well as dissociation of structure **2** into van der Waals complex **3** seems to be improbable in view of high-energy barriers on the reaction path.

We have also studied the possibility of dissociation of the hexagon-like structure **2** (**A**) into three isolated PN molecules by analogy with the dissociation of benzene into three acetylene molecules. On the first stage of the reaction as a result of removing opposite nitrogen and phosphor atoms from the plane of the molecule, the system takes the form of Dewar-like structure **4** (named **O** in Figure 4). This process requires overcoming the energy barrier of 33.2 kcal mol^{-1}. Therefore, cyclic isomer **A** (hexagon-like structure **2**) is kinetically "protected", which allows us to conclude that it could be kinetically stable under normal thermal conditions. Then, the rupture of P(terminal)−N(central) bond occurs, and via TS **P$_{TS}$**, the system converts into structure **Q**. The latter represents tetragon PNPN, one of the phosphor atoms of which is bound with the NP fragment oriented over the PNPN plane at an angle of 114°. This process as well as the previous one is endothermic. The subsequent elongation of the second P(terminal)−N(central) bond is accompanied by stabilization of the local minimum **S**. This process requires overcoming the energy barrier of 50 kcal mol^{-1}. Isomer **S** represents a planar structure in the form of a fork, in which three PN molecules locate at distances allowing the closest atoms of neighboring molecules to form P−N bonds (1.700 Å), the subsequent elongation of which results in the TS **T$_{TS}$** (see Figure S3). This structure is less stable at 91.3 kcal mol^{-1} than the hexagon-like structure **A**. The nitrogen atom of the central PN molecule deviates at 40° from the plane formed by the other five atoms. Gradient descent along the transition vector from the TS **T$_{TS}$** leads to the formation of a van der Waals complex between three isolated PN molecules **U**. Thus, the dissociation process of initial isomer **A** into three PN molecules is endothermic, and taking into account that the rearrangement of the **A** structure into three PN molecules requires overcoming 70−100 kcal mol^{-1} barriers, we think that our aromatic structure **A** is stable.

The DFT calculations are in good agreement with the results at the CCSD(T)/6-311+G(d) level of theory. The predicted difference in stabilization of van der Waals complexes **I** and **U** may be due to the correlation effects when we used the coupled cluster method.

The aromaticity of the planar hexagonal structure **2** is confirmed by the following findings. First of all, the high-symmetry structure and bond equalization are good indicators of that. Second, the N−P bond lengths in this structure—1.63 Å (PBE0/6-311+G*) and 1.64 Å (CCSD(T)/6-311+G*)—are very close to half of the double N=P bond in the HN=PH molecule: 1.58 Å (PBE0/6-311+G*) and 1.60 Å (CCSD(T)/6-311+G*) and the single N−P bond in the H$_2$N−PH$_2$ molecule: 1.71 Å (PBE0/6-311+G*) and 1.73 Å (CCSD(T)/6-311+G*). Next, we calculated the popular magnetic test of aromaticity—NICS$_{zz}$[32,33] at the PBE0/6-311+G* level of theory for both N$_3$P$_3$ and C$_6$H$_6$ molecules. Results of our calculations are summarized in Table 1 (h is a height in the NICS$_{zz}$ calculations).

In spite of the positive values of NICS$_{zz}$ at $h = 0$, negative values of the NICS$_{zz}$ index between $h = 0.8$ and 2.0 Å clearly indicate the deshielding and π-aromaticity in N$_3$P$_3$. One can see that benzene is more aromatic than our N$_3$P$_3$ molecule; though according to this criterion, it has almost a half of benzene's aromaticity. The maximum of the negative values of NICS$_{zz}$ occurs at 1.4 Å in N$_3$P$_3$ compared to 1.0 Å in C$_6$H$_6$. This fact can be explained by the larger atomic radius of phosphorus.

2.2. Aromatic N$_3$P$_3$ Molecule as a Ligand. Next, we computationally explore a possibility of the planar hexagonal

Table 1. NICS$_{zz}$ Index vs the Height of the Molecule Plane for C$_6$H$_6$ and N$_3$P$_3$

	NICS$_{zz}$	
h (Å)	C$_6$H$_6$	N$_3$P$_3$
0.0	−14.5	10.8
0.2	−16.5	9.3
0.4	−20.9	5.3
0.6	−25.6	0.3
0.8	−28.8	−4.2
1.0	−29.7	−7.6
1.2	−28.7	−9.6
1.4	−26.4	−10.3
1.6	−23.5	−10.2
1.8	−20.5	−9.6
2.0	−17.6	−8.8

N$_3$P$_3$ molecule to be a new ligand in chemistry. We selected the N$_3$P$_3$CrN$_3$P$_3$ molecule for this test because dibenzenechromium C$_6$H$_6$CrC$_6$H$_6$ sandwich complex is well-known in chemistry.[34] Indeed we found that the sandwich structure of the N$_3$P$_3$CrN$_3$P$_3$ molecule is the minimum (see Figure 5).
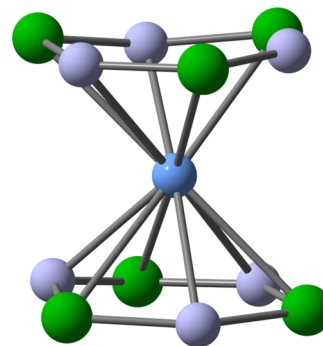
N$_3$P$_3$CrN$_3$P$_3$

Figure 5. Optimized sandwich structure of the N$_3$P$_3$CrN$_3$P$_3$ molecule.

There are very small distortions from planarity of the N$_3$P$_3$ ring upon the formation of this sandwich structure (see Figure S4), but it looks like the N$_3$P$_3$ ring is well-preserved. Therefore, we believe that the aromatic N$_3$P$_3$ molecule could be a potential new ligand in inorganic chemistry.

3. CONCLUSIONS

We computationally assessed the viability of the aromatic N$_3$P$_3$ molecule with a planar hexagonal structure. According to the calculations, this isomer is slightly thermodynamically unstable toward dissociation into a van der Waals complex between NP$_3$ distorted tetrahedron and N$_2$ molecule but is kinetically protected by high energy barriers of the nearest TSs, which allows us to suggest its existence under normal thermal conditions. The aromatic nature of the planar hexagonal structure is confirmed by calculations of the magnetic index NICS$_{zz}$ and N−P bond equalization. The calculations of the modeling of N$_3$P$_3$CrN$_3$P$_3$ sandwich complex indicate a possibility of using the N$_3$P$_3$ molecule as a potential ligand in chemistry.

4. METHODS

First, we performed a machine search for the global minimum structure for the N_3P_3 stoichiometry. The Coalescence-Kick method[35] for global minimum searches with subsequent geometry optimization using the Gaussian 09 program[36] was employed. Extensive searches (5000 trial structures) for singlet configurations were conducted at the PBE0[37]/3-21G[38] level of theory to explore the potential energy surface of the N_3P_3 stoichiometry. The low-lying isomers ($\Delta E \leq 30$ kcal mol^{-1}) were recalculated with geometry optimization and frequency calculations using a more extended 6-311+G** basis set.[39] Single-point calculations were performed at three levels of coupled cluster method (CCSD(T)[40,41]/6-311+G**, CCSD-(T)/aug-cc-pVTZ,[42] and CCSD(T)/aug-cc-pVQZ) to determine a more precise relative energy ordering. We also preformed PBE0/6-311+G* calculations in the search for the dissociation path of the planar hexagon structure into the lowest energy structure, which is a van der Waals complex of N_2 molecule and distorted tetrahedron P_3N. Single-point calculations for all TSs and LMs along the dissociation path were recalculated at the CASSCF(18,12)[43]/6-311+G* and CCSD-(T)/6-311+G* levels of theory to ensure that the wave function was tested for the multiconfiguration character. CASSCF(18,12) calculations include nine upper occupied and three LUMOs. To confirm that the found TSs belong to the studied reaction path, the method[44] of steepest descent (gradient motion) from the saddle point to the neighbor stationary point (saddle or minimum) has been performed for all the TSs and intermediates.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01719.

> Optimized structures and relative energies of N_3P_3, mechanism of intramolecular rearrangements of hexagon-like structure 2, mechanism of dissociation of hexagon-like structure 2, optimized sandwich structure of the $N_3P_3CrN_3P_3$ molecule, coordinates for N_3P_3: PBE0/6-311+G*, standard orientation, and total energies (a.u.) and relative energies corrected for ZPE (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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