Electronic Supplementary Information

Planar tetracoordinate carbon in boron-based cluster CB_4S_6 stabilized by peripheral bridging sulfur atoms

Cheng-Kai Liang, Guojuan Zhang and Rui Sun *

[1] Basic science Department, Shanxi Agricultural University, 1 Mingxian South Road, Jinzhong, Shanxi, 030801, People's Republic of China.

*To whom correspondence should be addressed.

E-mail: sunrui@sxau.edu.cn.

Contents

Cartesian Coordinates for the structures.

Computational methods

The designed CB_4S_6 cluster was optimized at both the B3LYP/aug-cc-pVTZ and B2PLYP[1]-D3(BJ)[2]/aug-cc-pVTZ levels, yielding nearly identical structures and vibrational frequencies. Furthermore, the wavefunction of the CB_4S_6 cluster was demonstrated to be stable at both computational levels. The potential energy surfaces (PESs) searches for the CB_4S_6 cluster were explored using the combination of stochastic search algorithm[3] and the Basin-hopping algorithm[4]. Both singlet and triplet states were considered during the search. Based on the energy ordering of the randomly generated initial structures (optimized at the PBE[5]/DZVP[6] level), the 15 lowest isomers were calculated at the B2PLYP-D3(BJ)/aug-cc-pVTZ level. Among these, the 10 lowest isomers were subsequently refined at the CCSD(T)/aug-cc-pVTZ level. The relative energies of the isomers were compared based on the CCSD(T)/aug-cc-pVTZ energies plus the B2PLYP-D3(BJ)/aug-cc-pVTZ zero-point energy corrections. To investigate the dynamic stability, Born-Oppenheimer molecular dynamics (BOMD) simulations were carried out at the PBE/DZVP level using the CP2K package[7]. Furthermore, the adaptive natural density partitioning (AdNDP)[8] analyses were performed using the AdNDP program[9] to discuss chemical bonding. Nucleus independent chemical shift (NICS)[10] calculations were done to assess π/σ aromaticity. Vertical detachment energies (VDEs) and vertical electron affinities (VEAs) were calculated using the outer valence Green's function (OVGF) procedure at the OVGF/aug-cc-pVTZ level.[11] The cross sections of NICS (CS-NICS) were generated with the Multiwfn 3.8 code,[12] CCSD(T) calculations were carried out using the MolPro 2012.1 package,[13] and all other calculations were performed using the Gaussian 16 package.[14]

Reference

1 S. Grimme, *J. Chem. Phys.*, 2006, **124**, 034108.

2 (a) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104; (b) S. Grimme, S. Ehrlich and L Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465.

3 (a) M. Saunders, *J. Comput. Chem*., 2004, **25**, 621–626; (b) P. P. Bera, K. W. Sattelmeyer, M. Saunders, H. F. Schaefer and P. v. R. Schleyer, *J. Phys. Chem. A*, 2006, **110**, 4287–4290.

4 D. J. Wales and H. A. Scheraga, *Science*, 1999, **285**, 1368–1372.

5 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett*., 1996, **77**, 3865–3868.

6 J. VandeVondele and J. Hutter, *J. Chem. Phys*., 2007, **127**, 114105.

7 T. D. Kühne and J. Hutter, *J. Chem. Phys.*, 2020, **152**, 194103.

8 D. Y. Zubarev and A. I. Boldyrev, *Phys. Chem. Chem. Phys*., 2008, **10**, 5207–5217.

9 The AdNDP program was downloaded freely at http://ion.chem.usu.edu/~boldyrev/adndp.php.

10 (a) P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. J. Jiao and N. Hommes, *J. Am. Chem. Soc*., 1996, **118**, 6317–6318; (b) Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta and P. v. R. Schleyer, *Chem. Rev.,* 2005, **105**, 3842–3888.

11 J. V. Ortiz, V. G. Zakrzewski and O. Dolgounircheva, Conceptual Perspectives in Quantum Chemistry, Kluwer Academic, 1997.

12 T. Lu and F. W. Chen, Multiwfn: A Multifunctional Wavefunction Analyzer. *J. Comput. Chem.,* 2012, **33**, 580–592.

13 H. J. Werner, *et al*. in MolPro 2012.1, University College Cardiff Consultants Limited, Cardiff U.K., 2012.

14 M. J. Frisch, et al. *Gaussian 16 Rev. A.03*, Wallingford, CT, 2016.

Table S1. Relative energies (ΔE) between the global minimum (**1**) of CB_4S_6 and its second lowest-lying isomer (**1a**) at different theoretical levels.

Theoretical levels	ΔE (kcal/mol)
CCSD(T)/aug-cc-pVTZ//B3LYP/aug-cc-pVTZ	4.6
CCSD(T)/aug-cc-pVTZ//TPSSh/aug-cc-pVTZ	4.6
CCSD(T)/aug-cc-pVTZ//PBE0-D3(BJ)/aug-cc-pVTZ	4.7
CCSD(T)/def2-TZVPP//PBE0-D3(BJ)/def2-TZVPP	4.5
CCSD(T)/aug-cc-pVDZ//B2PLYP-D3(BJ)/aug-cc-pVDZ	4.5
CCSD(T)/aug-cc-pVQZ//B2PLYP-D3(BJ)/aug-cc-pVQZ	4.5

Table S2. T1-Diagnostic values for the lowest-lying isomers of CB_4S_6 shown in Fig. 1.

Systems	**1**	**1a**	**1b**	**1c**	**1d**
T1 Diagnostic	0.018	0.018	0.018	0.018	0.019

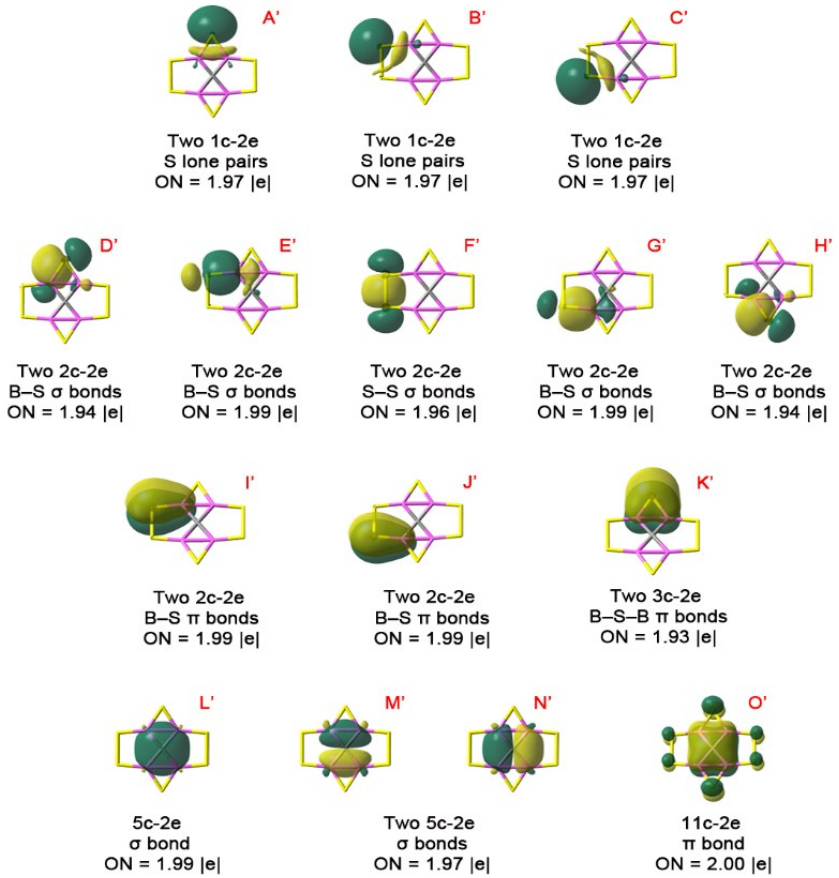

Fig. S1 AdNDP view of chemical bonding in the **1a** with occupation numbers (ONs) indicated.

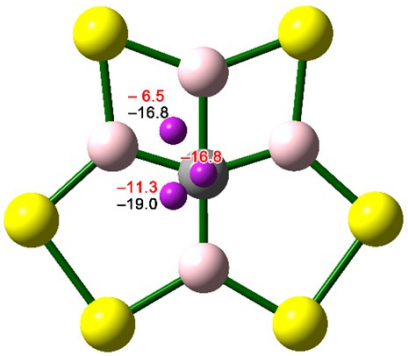

Fig. S2 Nucleus independent chemical shifts (NICSs) for the CB_4S_6 cluster. NICS (0), shown in black, is calculated at the center of a triangle. NICS (1), shown in red, is calculated at 1 Å above the center of the triangle and above the C center.

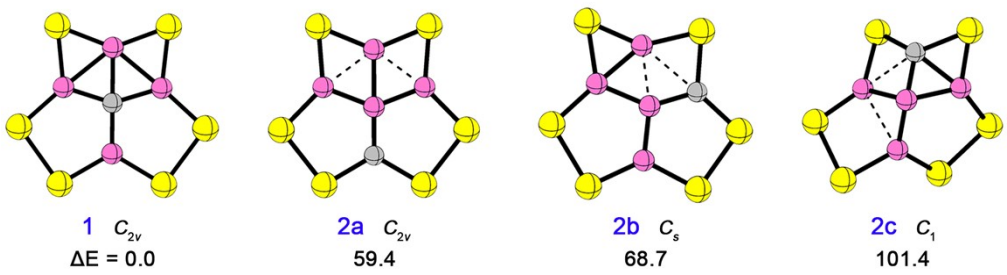

Fig. S3 Optimized structures of CB_4S_6 containing ptC or ptB at the B2PLYP-D3(BJ)/aug-cc-pVTZ level and the relative energies (ΔE, in kcal/mol) are reported at the CCSD(T) + $ZPE_{B2PLYP\text{-}D3(BJ)}$ level.

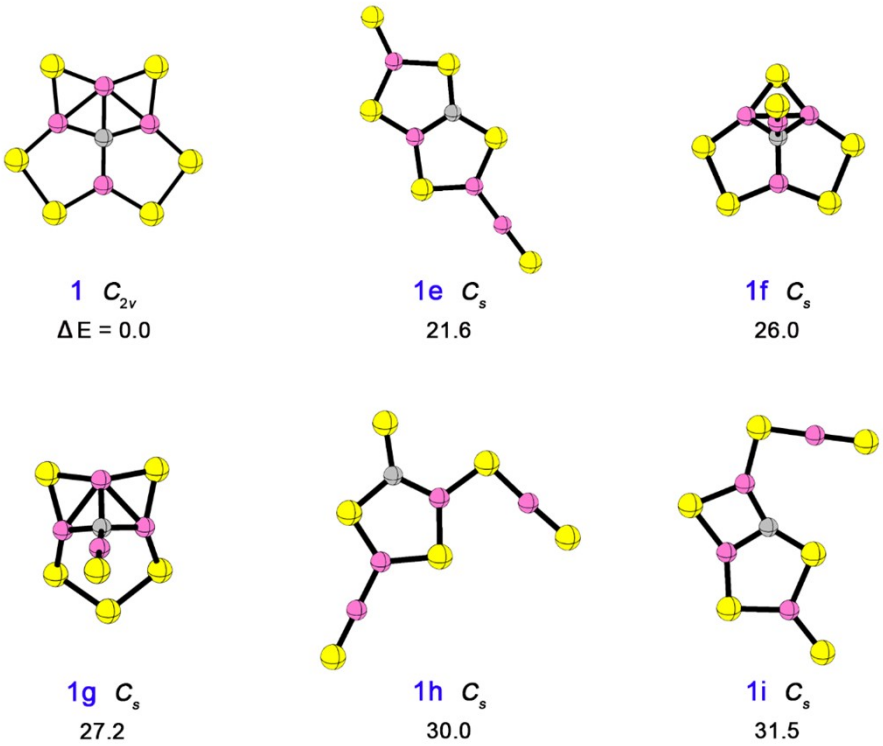

Fig. S4 Optimized structures of **1** and its five low-lying isomers (in addition to those shown in Fig. 1) at the B2PLYP-D3(BJ)/aug-cc-pVTZ level. The relative energies (ΔE, in kcal/mol) are reported at the CCSD(T) + $ZPE_{B2PLYP\text{-}D3(BJ)}$ level.

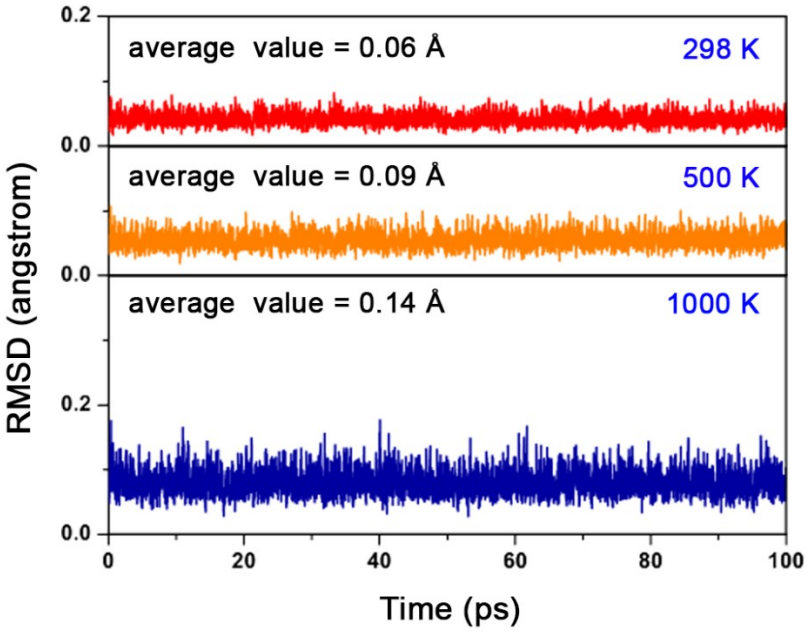

Fig. S5 RMSD vs time for BOMD simulations of **1a** at the PBE/DZVP level and at 298, 500, and 1000 K.

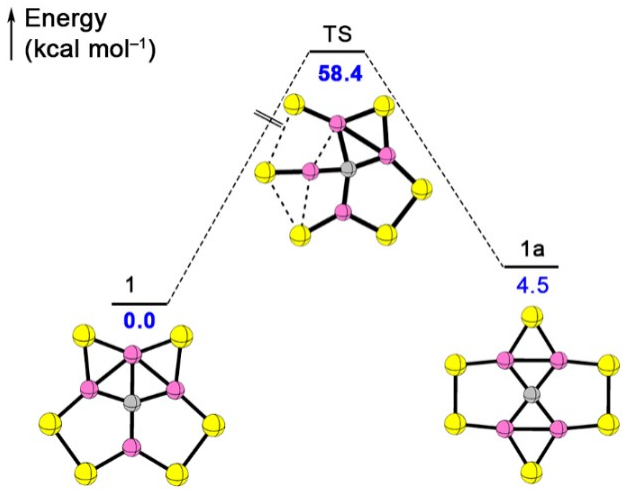

Fig. S6 Energy profiles for isomerization from **1** to **1a** via the TS. The relative energies (in kcal/mol) are compared at the CCSD(T) + $ZPE_{B2PLYP\text{-}D3(BJ)}$ level.

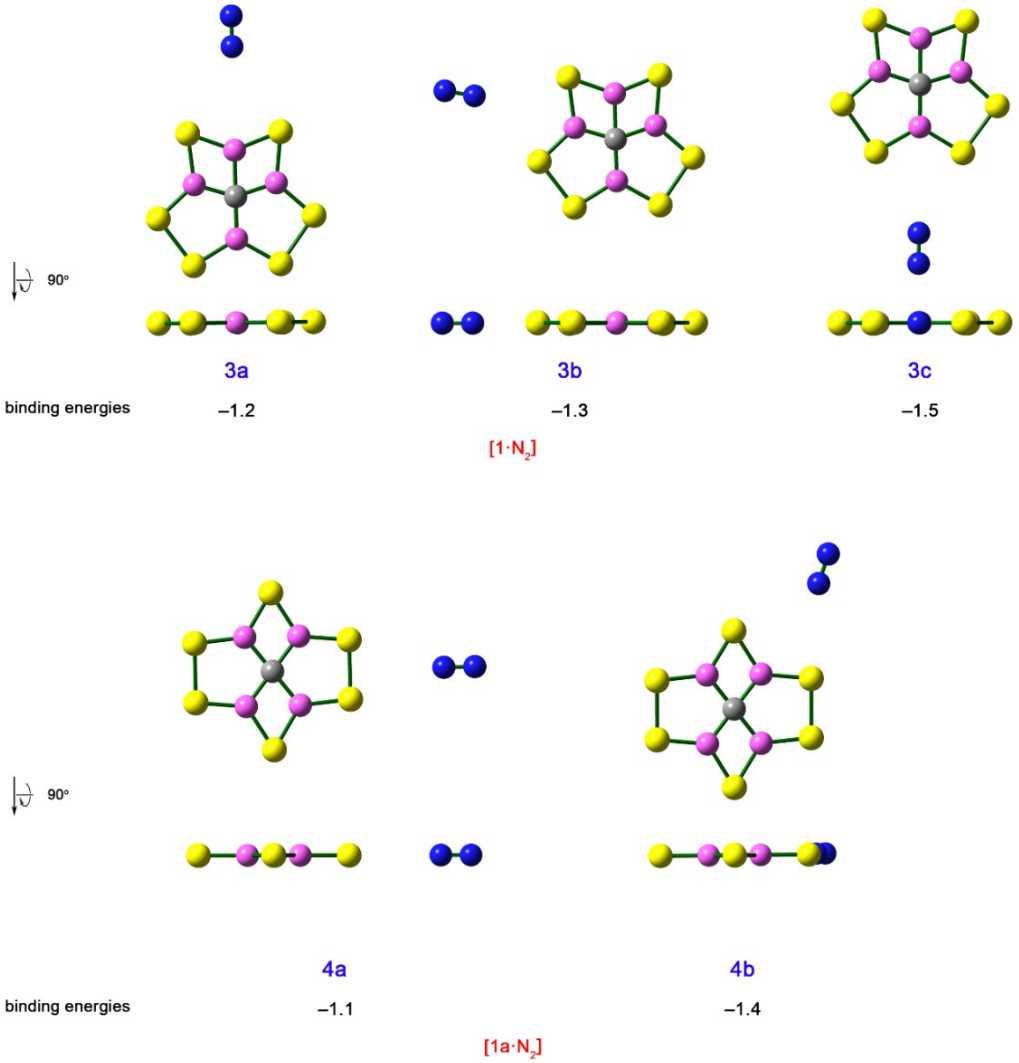

Fig. S7 Optimized structures of [**1**·N_2] and [**1a**·N_2] at the B2PLYP-D3(BJ)/aug-cc-pVTZ level and the corresponding binding energies.

Cartesian Coordinates for the structures.

Cartesian Coordinates of optimized structures shown in Fig. 1 and Fig S4 at the B2PLYP-D3(BJ)/aug-cc-pVTZ level.

0

B	-0.97839500	0.97839500	0.32771600
B	0.97839500	0.97839500	0.32771600
B	-0.97839500	-0.97839500	0.32771600
B	0.97839500	-0.97839500	0.32771600
C	0.00000000	0.00000000	1.03535000
S	0.00000000	2.44055400	-0.19947500
S	2.44055400	0.00000000	-0.19947500
S	0.00000000	-2.44055400	-0.19947500
S	-2.44055400	0.00000000	-0.19947500

1

C	0.00000000	0.00000000	0.19154800
B	0.00000000	0.00000000	1.85277200
B	0.00000000	0.00000000	-1.33459600
B	0.00000000	1.47643600	0.64927800
B	0.00000000	-1.47643600	0.64927800
S	0.00000000	-1.67021900	2.48376900
S	0.00000000	-2.80282400	-0.55012700
S	0.00000000	-1.56640700	-2.25342200
S	0.00000000	2.80282400	-0.55012700
S	0.00000000	1.56640700	-2.25342200
S	0.00000000	1.67021900	2.48376900

1a

C	0.00000000	0.00000000	0.00000000
B	0.00000000	0.95858500	1.22779300
B	0.00000000	-0.95858500	-1.22779300
B	0.00000000	0.95858500	-1.22779300
B	0.00000000	-0.95858500	1.22779300
S	0.00000000	0.00000000	2.78385400
S	0.00000000	0.00000000	-2.78385400
S	0.00000000	2.74502200	1.05449900
S	0.00000000	2.74502200	-1.05449900
S	0.00000000	-2.74502200	1.05449900
S	0.00000000	-2.74502200	-1.05449900

1b

C	0.01611600	0.47078600	0.00000000
B	0.65742900	1.60483000	0.92064800

B	-0.05776500	-0.20581300	-1.36157500
B	-0.05776500	-0.20581300	1.36157500
B	0.65742900	1.60483000	-0.92064800
S	1.25351300	3.04686200	0.00000000
S	0.65742900	0.96436900	-2.60930200
S	-0.58224200	-1.90135900	-1.68759200
S	-0.58224200	-1.90135900	1.68759200
S	-1.78472000	-2.22381200	0.00000000
S	0.65742900	0.96436900	2.60930200

1c

C	-0.79563600	0.01129600	0.00000000
B	-0.36954200	0.69762900	1.30195900
B	0.16438700	-1.27493800	-1.04281700
B	0.16438700	-1.27493800	1.04281700
B	-0.36954200	0.69762900	-1.30195900
S	0.16340200	2.40439100	1.06305500
S	0.16340200	2.40439100	-1.06305500
S	-0.01892300	-0.44562400	-2.67659900
S	-1.43398200	-1.69327100	0.00000000
S	1.57160900	-1.86768100	0.00000000
S	-0.01892300	-0.44562400	2.67659900

1d

C	0.06485600	0.05871900	0.53689300
B	-1.04741800	1.12180200	0.34306500
B	1.66322900	-0.64262800	0.06832000
B	-0.38083900	-1.34572900	-0.01510500
B	0.81814700	1.25180500	-0.39527600
S	-0.24548500	2.69289600	-0.16070200
S	2.30592300	0.66462100	-1.15613300
S	1.39102700	-0.09726100	1.82769100
S	-2.14788000	-1.54072100	-0.29815800
S	1.04433500	-2.36424100	-0.40381900
S	-2.70134100	0.50229500	-0.01052700

1e

C	0.00000000	0.80107700	0.00000000
B	-2.63857600	1.38074900	0.00000000
B	3.35858800	-1.78080900	0.00000000
B	-0.75544500	-0.56834700	0.00000000
B	1.86207700	-1.08241200	0.00000000
S	-0.91955200	2.19346900	0.00000000
S	1.72454200	0.74734500	0.00000000

S	0.33653900	-2.03302800	0.00000000
S	-4.01651700	2.37111500	0.00000000
S	4.82260700	-2.45232900	0.00000000
S	-2.51844500	-0.48609600	0.00000000

1f

C	0.25868400	0.38340100	0.00000000
B	1.37362700	1.38421600	0.00000000
B	-0.87692200	0.64102900	1.03223500
B	-0.87692200	0.64102900	-1.03223500
B	0.60633300	-1.12025300	0.00000000
S	0.55277600	-1.87145200	-1.65733400
S	-2.09670600	1.55736300	0.00000000
S	-0.87692200	-0.45247800	-2.46599000
S	2.57732900	2.46359000	0.00000000
S	0.55277600	-1.87145200	1.65733400
S	-0.87692200	-0.45247800	2.46599000

1g

C	0.71480500	0.32943700	0.00000000
B	0.39421100	1.84283700	0.00000000
B	-0.20484300	0.38136100	1.28244000
B	2.00254000	-0.41786400	0.00000000
B	-0.20484300	0.38136100	-1.28244000
S	3.40781600	-1.22012600	0.00000000
S	-1.04039600	-2.14253300	0.00000000
S	-0.20484300	2.17192700	1.71026700
S	-0.20484300	2.17192700	-1.71026700
S	-1.42337200	-0.89419500	1.65210400
S	-1.42337200	-0.89419500	-1.65210400

1h

C	-1.58088200	0.92854700	0.00000000
B	2.51094000	2.06155600	0.00000000
B	-0.70875000	-1.61833400	0.00000000
B	-0.69362400	-3.27102100	0.00000000
B	0.00000000	0.95226400	0.00000000
S	0.81462800	2.57055500	0.00000000
S	0.83493700	-0.64777100	0.00000000
S	-2.26192700	-0.71402200	0.00000000
S	-0.68115700	-4.88163200	0.00000000
S	-2.53231900	2.25276600	0.00000000
S	4.07224200	1.65800400	0.00000000

1i

C	0.00000000	0.29843800	0.00000000
B	1.12102400	1.35580800	0.00000000
B	-3.15920100	-0.33866700	0.00000000
B	2.33117900	-1.02176100	0.00000000
B	-1.11404400	1.38315300	0.00000000
S	0.00534700	2.84567900	0.00000000
S	3.33398600	-2.39501800	0.00000000
S	2.79630700	0.81044200	0.00000000
S	0.43353300	-1.28690800	0.00000000
S	-2.92206700	1.41703000	0.00000000
S	-3.39053000	-1.93392900	0.00000000

Cartesian Coordinates of optimized structures shown in Fig. S3 at the B2PLYP-D3(BJ)/aug-cc-pVTZ level.

1

C	0.00000000	0.00000000	0.19154800
B	0.00000000	0.00000000	1.85277200
B	0.00000000	0.00000000	-1.33459600
B	0.00000000	1.47643600	0.64927800
B	0.00000000	-1.47643600	0.64927800
S	0.00000000	-1.67021900	2.48376900
S	0.00000000	-2.80282400	-0.55012700
S	0.00000000	-1.56640700	-2.25342200
S	0.00000000	2.80282400	-0.55012700
S	0.00000000	1.56640700	-2.25342200
S	0.00000000	1.67021900	2.48376900

2a

B	0.00000000	0.00000000	-1.84683100
B	0.00000000	1.53114100	-0.70960500
S	0.00000000	1.67152500	-2.53707500
S	0.00000000	2.79128300	0.57857800
S	0.00000000	1.50216400	2.23362000
S	0.00000000	-2.79128300	0.57857800
S	0.00000000	-1.50216400	2.23362000
S	0.00000000	-1.67152500	-2.53707500
B	0.00000000	0.00000000	-0.11592900
B	0.00000000	-1.53114100	-0.70960500
C	0.00000000	0.00000000	1.35098100

2b

B	-1.42907800	-1.28810200	0.00000000

B	1.01457500	1.07622900	0.00000000
B	-1.57176600	0.45494100	0.00000000
S	-3.06971600	-0.64850500	0.00000000
S	-1.65434900	2.24440100	0.00000000
S	0.39675500	2.76852400	0.00000000
S	2.40372900	-1.53801700	0.00000000
S	2.75733000	0.54082900	0.00000000
S	-0.47588500	-2.83477300	0.00000000
C	0.70092000	-1.47132400	0.00000000
B	0.00000000	-0.18134700	0.00000000

2c

B	-1.69379600	-0.49357700	-0.38655600
S	-2.98880300	0.73373900	-0.72595900
S	-1.60774800	-2.01531800	0.54278400
S	0.48930900	-2.24492300	0.48329300
S	2.50123000	1.29623200	0.27484200
S	2.77223100	-0.54557700	-0.75115700
S	-0.61181100	2.28831900	0.84395600
B	-0.22852600	0.23596900	-0.89330500
B	0.73223300	1.22501600	0.21890500
C	-1.26967900	1.17938100	-0.45278400
B	0.93959800	-0.82257800	-0.53253100

Cartesian Coordinates of optimized structures shown in Fig. S7 at the B2PLYP-D3(BJ)/aug-cc-pVTZ level.

3a

C	0.00000000	0.00000000	-0.43802600
B	0.00000000	0.00000000	1.22581000
B	0.00000000	0.00000000	-1.96454600
B	0.00000000	1.47680800	0.02027200
B	0.00000000	-1.47680800	0.02027200
S	0.00000000	-1.67051900	1.85394700
S	0.00000000	-2.80268700	-1.18068000
S	0.00000000	-1.56688200	-2.88319600
S	0.00000000	2.80268700	-1.18068000
S	0.00000000	1.56688200	-2.88319600
S	0.00000000	1.67051900	1.85394700
N	0.00000000	0.00000000	4.93859500
N	0.00000000	0.00000000	6.03809800

3b

C	0.00000000	0.57947900	0.00000000
B	-1.66299900	0.54170600	0.00000000
B	1.52601000	0.62135400	0.00000000
B	-0.49542400	2.04433000	0.00000000
B	-0.41979600	-0.90936600	0.00000000
S	-2.24839200	-1.14392100	0.00000000
S	0.81738600	-2.20326400	0.00000000
S	2.48482800	-0.92057100	0.00000000
S	0.66937900	3.40190600	0.00000000
S	2.40364700	2.21145900	0.00000000
S	-2.33390200	2.19612900	0.00000000
N	-1.76470600	-5.65884700	0.00000000
N	-1.58187700	-4.57469500	0.00000000

3c

C	0.00000000	0.00000000	-0.77625400
B	0.00000000	0.00000000	-2.44057700
B	0.00000000	0.00000000	0.75171100
B	0.00000000	1.47568500	-1.23704200
B	0.00000000	-1.47568500	-1.23704200
S	0.00000000	-1.66956400	-3.07180600
S	0.00000000	-2.80301000	-0.03988000
S	0.00000000	-1.57128600	1.66585700
S	0.00000000	2.80301000	-0.03988000
S	0.00000000	1.57128600	1.66585700
S	0.00000000	1.66956400	-3.07180600
N	0.00000000	0.00000000	4.57449200
N	0.00000000	0.00000000	5.67391200

4a

C	0.00000000	0.00000000	-0.68397900
B	0.00016900	1.22708000	0.27643100
B	0.00000800	-1.22838600	-1.64141900
B	-0.00016900	-1.22708000	0.27643100
B	-0.00000800	1.22838600	-1.64141900
S	0.00020300	2.78384200	-0.68232600
S	-0.00020300	-2.78384200	-0.68232600
S	0.00014700	1.05395700	2.06290800
S	-0.00014700	-1.05395700	2.06290800
S	0.00000000	1.05410800	-3.42867100
S	0.00000000	-1.05410800	-3.42867100
N	0.00000000	0.00000000	5.39975100
N	0.00000000	0.00000000	6.49919000

4b

C	0.59480100	0.10326500	0.00007300
B	0.84645900	1.64108000	-0.00008800
B	0.35016000	-1.43545000	0.00010600
B	-0.95920200	-0.02719800	0.00033300
B	2.14762300	0.23735700	-0.00007600
S	2.63906200	1.99716100	-0.00025100
S	-1.44188100	-1.78959500	0.00045100
S	-0.49502400	2.83301900	-0.00000300
S	-2.04508800	1.40404800	0.00038600
S	3.23739800	-1.18972700	-0.00017600
S	1.69413100	-2.62574100	-0.00002800
N	-4.70832800	-0.68252400	0.00013700
N	-5.70761100	-1.14106800	-0.00126100