Electronic Supplementary Information

Planar pentacoordinate carbon in a sulphur-surrounded boron wheel: The global minimum of $CB_5S_5^+$

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Computational methods

The $CB_5S_5^+$ cluster and its concerned isomers were optimized at both B3LYP/aug-cc-pVTZ and B2PLYP-D3(BJ)/aug-cc-pVTZ levels, which gave almost identical structures and similar vibrational frequencies, so B2PLYP-D3(BJ) results geometries were reported in the text and used for energy improvement at the CCSD(T)/aug-cc-pVTZ level, while the B3LYP functional was used in various electronic structure analyses. The potential energy surface (PES) of $CB_5S_5^+$ was explored using the stochastic search algorithm.[1] Randomly generated initial structures were first optimized at the B3LYP/6-31G(d) level. Then ten lowest isomers were re-optimized and vibrational frequencies analyzed at B2PLYP-D3(BJ)/aug-cc-pVTZ. The energies of six lowest isomers were refined by single-point CCSD(T)/aug-cc-pVTZ calculations. The relative stabilities of isomers were determined by CCSD(T)/aug-cc-pVTZ energies with zero-point energy (ZPE) corrections at B2PLYP-D3(BJ)/aug-cc-pVTZ. Born-Oppenheimer molecular dynamic (BOMD) simulations were carried out to assess dynamic stability at the PBE/DZVP level, using the CP2K package.[2] Vertical detachment energies (VDEs) and vertical electron affinities (VEAs) were calculated using the outer valence Green's function (OVGF) procedure[3] at the OVGF/aug-cc-pVTZ level. Adaptive nature density partitioning (AdNDP)[4] analyses were performed at B3LYP/6-31G(d). Natural bond orbital (NBO)[5] and Nucleus independent chemical shifts (NICS)[6] analyses were performed at B3LYP/aug-cc-pVTZ level. The stochastic search algorithm was realized using the GXYZ 2.0 program,[7] AdNDP analysis was done using the AdNDP program,[8] and cross sections of NICS (CS-NICS) were generated with the Multiwfn 3.8 code.[9] The CCSD(T) calculations were carried out using the MolPro 2012.1 package,[10] NBO analyses were performed using NBO 3.1[11] and all other calculations were performed using the Gaussian 16 package.[12]

Reference

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Cartesian Coordinates for the structures shown in Fig. 1.

B3LYP/aug-cc-pVTZ-optimized structures for structures shown in Fig. 1.

0

C	0.00000000	0.00000000	0.58333900
B	0.00000000	1.54169200	0.09425400
B	1.46623700	0.47640900	0.09425400
B	-1.46623700	0.47640900	0.09425400
B	0.90618400	-1.24725500	0.09425400
B	-0.90618400	-1.24725500	0.09425400
O	-1.32841700	1.82841000	-0.14640900
O	-2.14942400	-0.69839000	-0.14640900
O	1.32841700	1.82841000	-0.14640900
O	2.14942400	-0.69839000	-0.14640900
O	0.00000000	-2.26003900	-0.14640900

1a

C	0.00000000	0.00000000	0.00000000
B	0.00000000	1.64814400	0.00000000
B	1.56747800	0.50930500	0.00000000
B	-1.56747800	0.50930500	0.00000000
B	0.96875500	-1.33337700	0.00000000
B	-0.96875500	-1.33337700	0.00000000
S	-1.66959500	2.29800000	0.00000000
S	-2.70146100	-0.87775800	0.00000000
S	1.66959500	2.29800000	0.00000000
S	2.70146100	-0.87775800	0.00000000
S	0.00000000	-2.84048400	0.00000000

1b

B	-0.05342000	0.39896400	1.83152200
B	0.13742800	-1.20120100	1.15211100
B	-0.05342000	0.39896400	-1.83152200
B	0.13742800	-1.20120100	-1.15211100
S	-0.05342000	-0.96250100	2.93621700
S	0.17733200	-2.60602500	0.00000000
S	-0.09582900	2.21003800	1.63254700
S	-0.09582900	2.21003800	-1.63254700
S	-0.05342000	-0.96250100	-2.93621700
C	0.04868000	1.54950100	0.00000000
B	0.16130100	0.10011800	0.00000000

1c

C	0.00000000	0.00000000	0.16595100
B	0.00000000	1.36453900	-0.44543100
B	0.00000000	0.00000000	-2.50646700
B	0.00000000	0.93651600	1.49512900
B	0.00000000	-1.36453900	-0.44543100
B	0.00000000	-0.93651600	1.49512900
S	0.00000000	2.63814100	0.85659300
S	0.00000000	0.00000000	3.02564100
S	0.00000000	1.69224100	-2.33692500
S	0.00000000	-1.69224100	-2.33692500
S	0.00000000	-2.63814100	0.85659300

1d

C	0.00000000	0.00000000	0.36714300
B	0.00000000	1.43427800	-0.42497500
B	0.00000000	0.00000000	1.89649000
B	0.00000000	-1.43427800	-0.42497500
B	-1.43427800	0.00000000	-0.42497500
B	1.43427800	0.00000000	-0.42497500
S	0.00000000	0.00000000	3.49286200
S	1.72022100	-1.72022100	-0.92299400
S	-1.72022100	1.72022100	-0.92299400
S	-1.72022100	-1.72022100	-0.92299400
S	1.72022100	1.72022100	-0.92299400

B2PLYP-D3(BJ)/aug-cc-pVTZ-optimized structures for structures shown in Fig. 1.

0

C	0.00000000	0.00000000	0.59688400
B	0.00000000	1.53996400	0.09617100
B	1.46459300	0.47587500	0.09617100
B	-1.46459300	0.47587500	0.09617100
B	0.90516800	-1.24585700	0.09617100
B	-0.90516800	-1.24585700	0.09617100
O	-1.32873500	1.82884700	-0.14963900
O	-2.14993900	-0.69855800	-0.14963900
O	1.32873500	1.82884700	-0.14963900
O	2.14993900	-0.69855800	-0.14963900
O	0.00000000	-2.26058000	-0.14963900

1a

C	0.00000000	0.00000000	0.00000000
B	0.00000000	1.64428700	0.00000000
B	1.56381000	0.50811300	0.00000000
B	-1.56381000	0.50811300	0.00000000
B	0.96648800	-1.33025600	0.00000000
B	-0.96648800	-1.33025600	0.00000000
S	-1.66734700	2.29490600	0.00000000
S	-2.69782400	-0.87657600	0.00000000
S	1.66734700	2.29490600	0.00000000
S	2.69782400	-0.87657600	0.00000000
S	0.00000000	-2.83666000	0.00000000

1b

B	-0.08805800	0.40207600	1.80630000
B	0.25776700	-1.18950000	1.13716000
B	-0.08805800	0.40207600	-1.80630000
B	0.25776700	-1.18950000	-1.13716000
S	-0.08805800	-0.96896800	2.90060900
S	0.36309500	-2.5987470	0 0.00000000
S	-0.20326200	2.20274900	1.62771800
S	-0.20326200	2.20274900	-1.62771800
S	-0.08805800	-0.96896800	-2.90060900
C	0.06049100	1.56252400	0.00000000
B	0.29053200	0.11960600	0.00000000

1c

C	0.00000000	0.00000000	0.15889400
B	0.00000000	1.36650400	-0.44879000
B	0.00000000	0.00000000	-2.47948800
B	0.00000000	0.93590400	1.48909400
B	0.00000000	-1.36650400	-0.44879000
B	0.00000000	-0.93590400	1.48909400
S	0.00000000	2.63613600	0.85347800
S	0.00000000	0.00000000	3.01785800
S	0.00000000	1.69531900	-2.32987400
S	0.00000000	-1.69531900	-2.32987400
S	0.00000000	-2.63613600	0.85347800

1d

C	0.00000000	0.00000000	0.36930500
B	0.00000000	1.42938400	-0.42315300
B	0.00000000	0.00000000	1.89530100
B	0.00000000	-1.42938400	-0.42315300
B	-1.42938400	0.00000000	-0.42315300
B	1.42938400	0.00000000	-0.42315300
S	0.00000000	0.00000000	3.49471700
S	1.71670100	-1.71670100	-0.92413700
S	-1.71670100	1.71670100	-0.92413700
S	-1.71670100	-1.71670100	-0.92413700
S	1.71670100	1.71670100	-0.92413700