

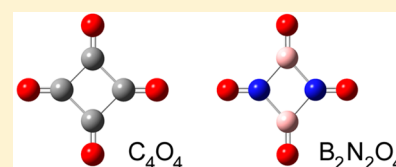
B₂N₂O₄: Prediction of a Magnetic Ground State for a Light Main-Group Molecule

Zoltan Varga* and Donald G. Truhlar*

Department of Chemistry, Chemical Theory Center, and Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455, United States

S Supporting Information

ABSTRACT: Cyclobutanetetrone, (CO)₄, has a triplet ground state. Here we predict, based on electronic structure calculations, that the B₂N₂O₄ molecule also has a triplet ground state and is therefore paramagnetic; the structure is an analogue of (CO)₄ in which the carbon ring is replaced by a (BN)₂ ring. Similar to (CO)₄, the triplet ground-state structure of B₂N₂O₄ is also thermodynamically unstable. Besides analysis of the molecular orbitals, we found that the partial atomic charges are good indicators for predicting magnetic ground states.



INTRODUCTION

Structures with stable magnetic spin states are important prospects for the development of functional materials.¹ Good candidates are provided by diradicals, which can be either triplets or open-shell singlets in their ground state.² Small magnetic molecules that do not contain transition metals or other heavy elements are especially interesting because of their light weight.

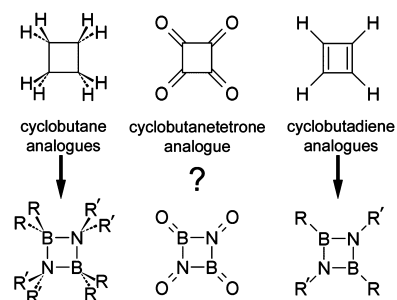
Cyclobutanetetrone, (CO)₄, is a particularly intriguing main-group molecule, having only eight atoms and a triplet ground state. The triplet-ground-state property was theoretically predicted³ and later confirmed by experimental studies.⁴ The molecular structures of the triplet ground state and singlet excited states are square-planar with *D*_{4h} symmetry, which led to some exploration for similar molecules with triplet ground states, but such searches failed so far.⁵ Some of the explored molecules [e.g., (CS)₄] keep the square-planar geometry, but the singlet spin state is preferred; others [e.g., (SiO)₄] undergo a geometry change to tetrahedral, where again the singlet spin state is preferred; in yet other cases [e.g., (PN)₄], the structure just falls apart into smaller fragments.^{5c} These examples involve substitution of either just the ring or the exocyclic atoms or both types of atoms into the (CO)₄ molecule. In the present Article, we predict that another molecule with a triplet ground state can be found by making substitutions in the ring atoms with the exocyclic atoms unchanged.

In organic chemistry, one can generally distinguish two types of four-membered rings. The first are rings like the saturated cyclobutane structure, (CH₂)₄, where the carbon atoms are connected by single bonds and the ring is bent; see ref 6 and references cited therein. A carbon ring with a triplet spin state is very unlikely for such a structure. The second kind of ring is exemplified by cyclobutadiene, (CH)₄, where the four π electrons lead, by Hückel's $4n + 2$ rule, to an antiaromatic character.⁷ The square-planar structure leads to degenerate partially bonding (but often called nonbonding) π orbitals with e_g symmetry, and Hund's rule predicts a triplet state. However,

according to the Jahn–Teller theorem, the molecule deforms to avoid degeneracy. In this case, the ground state is still planar, but rectangular rather than square, and it has alternating double and single bonds; see ref 8 and references cited therein. This rectangular ground state has a singlet spin state, and the square-planar triplet state is the first excited state, about 6 kcal/mol higher.

The carbon ring of (CO)₄ is intermediate between the above two cases. In contrast to the cycloalkanes, each carbon atom is connected to only one nonring atom. However, these connections are double bonds, instead of single bonds as in annulenes. Here we will explore whether other ring structures that are intermediate in this sense (see Scheme 1) can also lead to triplet ground states. Can we consider the intermediacy of the ring to be a key to its having a ground-state triplet?

Scheme 1



It is well-known that B–N bonds are similar to C–C bonds, with which they are isoelectronic.⁹ There are many examples of materials in which the carbon atoms are replaced by boron nitrides, for instance in nanotubes.¹⁰ Another example is provided by the aminoboranes, H₂N–BH₂, where substituents

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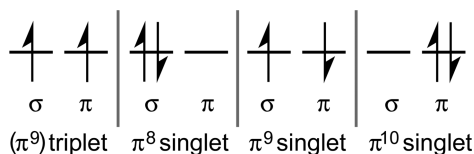
stabilize the structures. Such monomeric molecules tend to associate into oligomers; for example, two $\text{H}_2\text{N}-\text{B}(\text{Me})_2$ units can be reversibly cyclized into dimers, giving a cyclobutane-like analogue of aminoborane, although the ring is not puckered.⁹

Among the cyclic iminoboranes (molecules with dicoordinate boron and nitrogen atoms), the cyclic 1,3,2,4-diazadiboretidine, $\text{B}_2\text{N}_2\text{H}_4$, has been investigated by theoretical methods.¹¹ The B_2N_2 ring, similar to cyclobutadiene, has four π electrons, but because of the heteronuclear character of the ring, the symmetry is already decreased to a point group with no degenerate representations, and the structure has a closed-shell electronic state with no Jahn–Teller effect. The highest occupied molecular orbital (HOMO) in $\text{B}_2\text{N}_2\text{H}_4$ corresponds to two nonbonding π -type orbitals of nitrogen atoms, which act as lone pairs. Pyramidalization at the nitrogen atoms (as in ammonia) decreases repulsion of the HOMO and HOMO–4 orbitals, and this apparently makes up for the less favorable bonding between the π orbitals of the nitrogen and boron atoms; therefore, the ring puckers into a butterfly shape. Although $\text{B}_2\text{N}_2\text{H}_4$ itself has not been synthesized yet, derivatives are known¹² in which the ring is surrounded by bulky ligands (e.g., alkyl groups), and both planar and puckered $(\text{BN})_2$ rings can be formed.¹³

The analogies leading us to suspect that cyclic $\text{B}_2\text{N}_2\text{O}_4$ will show properties similar to $(\text{CO})_4$ are summarized in Scheme 1.

These $(\text{CO})_4$ -like systems have four low-lying electronic states (see Scheme 2), which have been studied previously, and

Scheme 2



we follow, in a slightly modified way, the previous literature for their discussion.^{3–5} In the triplet spin state, one of the singly occupied frontier orbitals has π character, while the other one is σ ; altogether this electronic state contains nine valence π electrons, and we denote this as a π^9 configuration, with similar notation for the other states. The open-shell singlet state has the same electron distribution, so it is called the π^9 singlet. The closed-shell singlet spin states have either a doubly occupied π orbital as the HOMO with a σ lowest unoccupied molecular orbital (LUMO) or vice versa; this leads to the notation of π^{10} singlet and π^8 singlet.

Intermediate-ring systems are expected to be very challenging for theoretical calculations because of near-degeneracy correlation effects. For example, it was recently shown^{3b} that even fourth-order single-reference perturbation theory is qualitatively inadequate to describe the electronic structures and energies of the states of $(\text{CO})_4$, although coupled-cluster theory, in particular CCSD(T), and Kohn–Sham density functional theory, in particular with the B3LYP functional, provided qualitatively acceptable results.^{3–5} However, the energy order of the low-lying electronic states still strongly depends on the theoretical method, and experimental investigation was required to decide between the two major scenarios.⁴ These results show that coupled-cluster methods give an energy ordering in reasonable agreement with experiment, whereas the B3LYP exchange–correlation func-

tional overestimates the energy gain of the triplet spin state over closed-shell singlets.

In the first part of this study, we discuss the relative energies of the triplet and singlet spin states of the $\text{B}_2\text{N}_2\text{O}_4$ molecule, and we compare the geometrical parameters to those of $(\text{CO})_4$. Then, the relative stability of the $\text{B}_2\text{N}_2\text{O}_4$ molecule will be predicted with comparison to the already synthesized $(\text{BN})_2$ -ring molecules. Finally, to extend the recent analysis in terms of molecular orbitals (MOs),⁵ we investigate the ability of the partial atomic charges and partial atomic magnetization (spin density) of the atoms to serve as alternative indicators for $(\text{CO})_4$ -like molecules.

COMPUTATIONAL METHODS

Geometry optimization and frequency calculations of all of the molecules were carried out by Kohn–Sham density functional theory with the M06 exchange–correlation functional.¹⁴ We performed spin-restricted, closed-shell calculations for the singlet states and spin-unrestricted calculations for open-shell singlet, doublet, and triplet spin states by using the *Gaussian 09* program package.¹⁵ The calculations were carried out with the *maug-cc-pVTZ* basis set.¹⁶

In order to better understand the physics associated with the almost degenerate energies of the frontier orbitals for the triplet spin state of $\text{B}_2\text{N}_2\text{O}_4$, vertical ionization energy (vIE) and vertical electron affinity (vEA) calculations were carried out by M06/*maug-cc-pVTZ* on the geometry of the triplet $\text{B}_2\text{N}_2\text{O}_4$.

The harmonic vibrational frequencies were calculated by the M06/*maug-cc-pVTZ* electronic structure model and scaled by the factor (0.996) recommended¹⁷ to improve their accuracy. Enthalpy calculations (when given below) are based on scaled harmonic vibrational frequencies calculated by M06/*maug-cc-pVTZ* and correspond to 0 K.

We analyzed the electronic structures by calculating the spin densities by the Hirshfeld scheme,^{18a} the partial atomic charges by the CM5 method,^{18b} and the bond indices by the Wiberg method.¹⁹

Geometry optimizations were carried out for the four (triplet, π^8 singlet, π^9 singlet, and π^{10} singlet) low-lying electronic states of $(\text{CO})_4$ and $\text{B}_2\text{N}_2\text{O}_4$ molecules by coupled-cluster calculations, CCSD(T),^{20,21} with the *maug-cc-pVTZ* basis set. To obtain the geometries of the triplet, π^8 singlet, and π^{10} singlet spin states, coupled-cluster calculations were carried out with the *Molpro* program package.²² In these calculations, we used a spin-restricted Hartree–Fock calculation as the reference, and the post-self-consistent-field coupled-cluster calculations were spin-unrestricted for the triplet states and spin-restricted for the two closed-shell singlet states (π^8 and π^{10}). For the open-shell singlet spin states (π^9), the geometry optimizations were carried out by the *Gaussian 09* program by using spin-unrestricted calculations. To ascertain the compatibility of these calculations, the optimized geometries of the π^8 states from *Molpro* calculations were reoptimized with *Gaussian 09*; they did not change. So, the relative energy of the π^9 singlet state can be calculated as an energy difference without further modification. In the CCSD(T) calculations, the T1 diagnostic values were checked to make sure that the wave function can be described reasonably well with a single reference configuration, and these diagnostics were found to be between 0.021 and 0.026. These values are somewhat larger than the multireference criterion suggested by Lee et al.,²³ but they indicate only moderate multireference character. Nevertheless, we carried out multireference calculations to further explore the nature of the wave functions for the investigated electronic states of $\text{B}_2\text{N}_2\text{O}_4$ [and $(\text{CO})_4$ as a reference]. These calculations are discussed in the multireference section of the Supporting Information (SI).

In addition to the above-mentioned M06, CCSD(T), and multireference calculations, we verified the ordering of the closed-shell singlet (π^8 and π^{10}) and triplet states of $\text{B}_2\text{N}_2\text{O}_4$ with an explicitly correlated basis set. In particular, CCSD(T)-F12b/*cc-pVTZ*-F12 calculations^{24–26} were carried out with *Molpro*.

RESULTS AND DISCUSSION

From (CO)₄ to B₂N₂O₄. We found that when the carbon atoms in (CO)₄ are replaced by a (BN)₂ ring, the triplet spin state remains energetically preferred over all three singlet states; see Table 1. For (CO)₄, both the CCSD(T)/maug-cc-pVTZ

Table 1. Comparison of the Low-Lying Excitations for (CO)₄ and B₂N₂O₄^a

molecule	method	triplet	π^8 singlet	π^9 singlet	π^{10} singlet
(CO) ₄ ^b		³ B _{1u}	¹ A _{1g}	¹ B _{1u}	¹ A _{1g}
	M06	0.0	11.7	4.8 ^c	7.1
	CCSD(T)	0.0	2.6	3.2	6.8
	CCSD(T)-F12b	0.0	2.8		6.6
	MRCI+Q ^d	0.0	-5.8	5.1	1.7
experiment ^e	0.0	1.5	3.2		
B ₂ N ₂ O ₄ ^f		³ A _u	¹ A _g	¹ A _u	¹ A _g
	M06	0.0	13.5	9.0 ^c	10.7
	CCSD(T)	0.0	1.5	7.8	1.1
	CCSD(T)-F12b	0.0	1.6		1.1
	MRCI+Q ^d	0.0	-11.0	7.1	-2.9

^aRelative energies in kilocalories per mole. ^bThe symmetry of the molecule is *D*_{4h}. ^cYamaguchi's spin projection was applied; for details, see the Computational Details section. ^dSingle-point energy calculation on the CCSD(T) geometries (for further details, see the multireference calculations section in the SI). ^eReference 4. ^fThe symmetry of the molecule is *D*_{2h}.

calculations and the explicitly correlated CCSD(T)-F12b/cc-pVTZ-F12 calculations agree well with the available experimental results. Among the M06 results, the energy gap for the triplet → π^9 singlet transition is described well compared to the experimental value and the coupled-cluster results. For the triplet → π^{10} singlet transition, there are no experimental values, but the M06 calculation agrees well with both coupled-cluster results. However, for the triplet → π^8 singlet transition, the M06 result overestimates the energy by about 10 kcal/mol compared to the experiment.

For the B₂N₂O₄ system, a slightly modified energy order is found; on the basis of the above validation study for (CO)₄, we assume that the energy order is well predicted by the coupled-cluster calculations. The triplet spin state is the ground state, but the first excited state is the π^{10} singlet. Then comes the other closed-shell singlet (π^8), followed by the open-shell singlet (π^9). The M06 calculations overestimate the energy of both the triplet → π^{10} singlet and triplet → π^8 singlet transitions by slightly more than 10 kcal/mol compared to the coupled-cluster results. However, the energy gap of the triplet

→ π^9 singlet agrees better with the coupled-cluster result; their difference is about 1 kcal/mol.

The *D*_{4h} symmetry of (CO)₄ decreases to *D*_{2h} in B₂N₂O₄, and the geometry changes are compared in Table 2. For the lower-energy triplet spin state, the bond angles of the ring atoms are changed by ±6–8° from the right angles of (CO)₄. The geometrical parameters of the four low-lying electronic states are very similar to each other; their difference is usually less than 0.01 Å and 2°. The bond lengths of CCSD(T) calculations are longer than those from M06 calculations by about 0.005–0.016 Å for both (CO)₄ and B₂N₂O₄.

Among the four states, the two closed-shell singlet states (π^8 and π^{10}) show the largest differences in their geometrical parameters, while the geometrical parameters of the triplet state are between the values of the two closed-shell singlets. When the doubly occupied HOMO orbital has σ character, the molecule is more extended, and when it is a π orbital, the molecule adopts a compact form. A reasonable way to compare these orbitals is provided by the triplet state in which they are both singly occupied; Figure 1 shows these orbitals for the

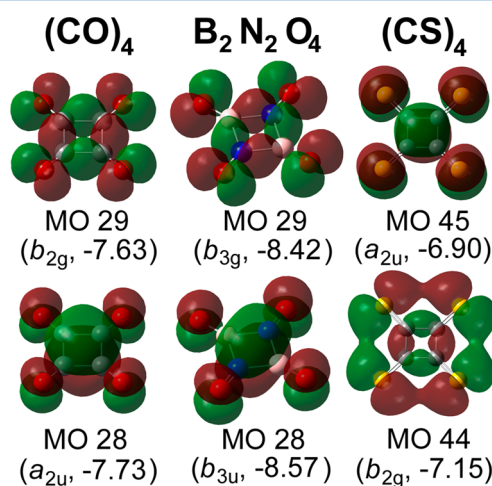


Figure 1. Singly occupied π and σ orbitals of the (CO)₄, B₂N₂O₄, and (SO)₄ molecules. [In parentheses are the symmetry and the energy (in electronvolts) of the orbital by M06/maug-cc-pVTZ.]

triplet (CO)₄ and B₂N₂O₄ molecules. The orbitals are similar in the two molecules, although the MOs of B₂N₂O₄ undergo a shape deformation that results in somewhat oval MOs because of the decreased symmetry. The same considerations that lead to Hund's rule predict that the triplet states are preferred when these two orbitals have very similar energies. For (CO)₄, their energy difference in the triplet is 0.10 eV, while we see a slightly

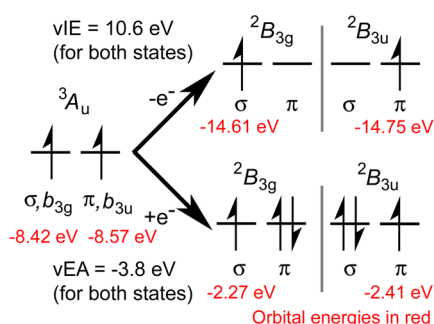
Table 2. Comparison of Molecular Geometries for the Low-Lying States of (CO)₄ and B₂N₂O₄

molecule	parameter	triplet		π^8 singlet		π^9 singlet		π^{10} singlet	
		M06	CCSD(T)	M06	CCSD(T)	M06	CCSD(T)	M06	CCSD(T)
(CO) ₄	<i>r</i> _{C–C} , Å	1.550	1.561	1.563	1.567	1.554	1.562	1.547	1.550
	<i>r</i> _{C–O} , Å	1.179	1.190	1.183	1.199	1.177	1.190	1.172	1.187
	α _{C–C–C} , deg	90.0	90.0	90.0	90.0	90.0	90.0	90.0	90.0
B ₂ N ₂ O ₄	<i>r</i> _{N–B} , Å	1.598	1.610	1.610	1.609	1.595	1.618	1.584	1.600
	<i>r</i> _{N–O} , Å	1.182	1.196	1.182	1.203	1.189	1.188	1.178	1.201
	<i>r</i> _{B–O} , Å	1.227	1.237	1.232	1.245	1.220	1.232	1.224	1.234
	α _{N–B–N} , deg	82.9	82.2	84.1	83.7	83.5	81.9	81.9	81.6
	α _{B–N–B} , deg	97.1	97.8	95.9	96.3	96.5	98.1	98.1	98.4

larger difference, 0.15 eV, for $B_2N_2O_4$. The figure also contains the orbital energies of triplet $(CS)_4$; for this molecule, the σ -type MO is energetically preferred over the π -type one, and their energy difference in the triplet is 0.25 eV. This larger splitting is consistent with the fact that, as already mentioned in the Introduction, $(CS)_4$ has a singlet ground state.

To verify the above-mentioned small energy difference between the two singly occupied MOs of triplet $B_2N_2O_4$, vIE, and vEA calculations were carried out by M06/maug-cc-pVTZ. In these calculations, the radical cation and radical anion of $B_2N_2O_4$ have doublet spin states, either of the $\pi(b_{3u})$ or $\sigma(b_{3g})$

Scheme 3



orbitals can be occupied (see Scheme 3). For each case (${}^3A_u \rightarrow {}^2B_{3u}$ or ${}^2B_{3g}$), we get the same vIE and vEA energies, 10.6 and -3.8 eV, respectively. Also, for both radical-cation and radical-anion calculations, the energy difference of the π and σ orbitals is 0.14 eV, which practically corresponds to the case of the triplet $B_2N_2O_4$.

Between the π^8 and π^{10} singlet states of $(CO)_4$, there is an energy difference of about 4 kcal/mol, while those two states are much closer in energy for $B_2N_2O_4$ (about 0.5 kcal/mol).

The B–N bond lengths of $B_2N_2O_4$ agree well with typical single B–N bond lengths (~ 1.6 Å from ref 9), as is the case for the C–C bonds in $(CO)_4$. These observations are supported by the Wiberg bond indices for the triplet $B_2N_2O_4$, where the N–B and C–C bonds in the corresponding molecules are 0.64 and 0.85, respectively. The distances of the B–O, N–O, and C–O bonds correspond well with typical double bonds (~ 1.2 Å for all three bonds from ref 9), and the double-bond character is confirmed by their Wiberg bond indices, which are 1.71, 1.71, and 1.82, respectively, for the triplet states.

The harmonic vibrational frequencies of all four states of $B_2N_2O_4$ are given in the SI (Table S3), where their IR intensities and Raman activities are also listed.

On the basis of the energetic ordering of the electronic states of $(CO)_4$, the predicted energetic ordering of states in $B_2N_2O_4$ is very convincing, although experimental studies are still required to verify the present predictions, and that leads to the next important question.

Is the $B_2N_2O_4$ Structure Stable? Is $B_2N_2O_4$ stable? The short answer is that, just like the triplet C_4O_4 molecule, it is not thermodynamically stable. Before details are given for $B_2N_2O_4$, it is instructive to first consider that



is exothermic by about 32 kcal/mol (by M06/maug-cc-pVTZ calculations in Table 3). However, such a direct dissociation, as was already shown in ref 5a, is forbidden by orbital symmetry

Table 3. Energy Difference (in kcal/mol) of Isoelectronic Systems of $B_2N_2O_4$ and the Dissociation Energy of $(CO)_4$ into CO Molecules by M06/maug-cc-pVTZ^a

system A	system B	ΔE_{B-A}
C_4O_4	4CO	–32.2
$B_2N_2O_4$	2OBNO	31.6
$B_2N_2O_4$	2BO + 2NO	122.2
$B_2N_2O_4$	2BO + N_2 + O_2	79.1
$B_2N_2O_4$	B_2O_2 + 2NO	6.4
$B_2N_2O_4$	B_2O_2 + N_2 + O_2	–36.7
$B_2N_2O_4$	O_2BOBO + N_2	–116.6
$B_2N_2O_4$	N_2O_3 + B_2O	127.1
$B_2N_2O_4$	singlet (BBNN) O_4	–4.3
$B_2N_2O_4$	singlet ON(B_2O_2)NO	–22.2
$B_2N_2O_4$	triplet ON(B_2O_2)NO	–11.2
$B_2N_2O_4$ + 4CH ₄	[(Me) ₂ BNH ₂] ₂ ^b + 2O ₂	38.1
$B_2N_2O_4$ + 4CH ₄	[H ₂ BN(Me) ₂] ₂ ^c + 2O ₂	88.0
$B_2N_2O_4$ + 2C ₃ H ₁₂ ^d	(MeBN- <i>t</i> -Bu) ₂ ^e + 2O ₂	38.1

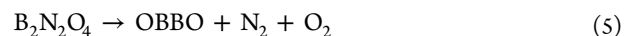
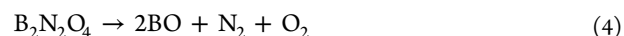
^aThe energy of the ground spin state was used for this table. The calculated geometries and electronic energies of all of the structures shown are available in the SI. ^bReference 9. ^cReference 30. ^dNeopentane as *t*-BuMe. ^eReference 31.

and leads to a very high barrier height, about 100 kcal/mol in energy (by CASPT2 calculations in the above reference).

The similar dissociation of triplet $B_2N_2O_4$ is



but this step is endothermic by 122.2 kcal/mol (by M06/maug-cc-pVTZ calculations). In the case of reaction 2 though, both the product molecules are radicals, and they can react further or other products could be formed directly, leading to the following possible net reactions:



Reactions 3, 4, and 7 are endothermic (by 6.4, 79.1, and 37 kcal/mol, respectively), but reactions 5 and 6, which both produce N_2 , are exothermic by 37 and 117 kcal/mol, respectively. However, because they require breaking of the B–N bonds of the ring, these reactions might be slow.

We can also consider the isomerization of $B_2N_2O_4$. The tetrahedral molecular arrangement is a reasonable one for these $(CO)_4$ analogues; for instance, $(SiO)_4$ and $(BF)_4$ have this arrangement.⁵ This tetrahedral arrangement was tested for both the π^8 and π^{10} corresponding singlet spin states of the planar $B_2N_2O_4$ structure. In each case, the tetrahedral initial structure optimized to a planar geometry.

Another isomer can be created by changing the sequence of the ring atoms from (BNBN) to (BBNN); see Figure 2. We optimized the geometry for both the singlet and triplet spin states of this rearranged (BBNN) O_4 isomer. For the singlet state, the B–B bond in the ring breaks (Figure 2b), and this isomer is lower in energy by 4.3 kcal/mol than the triplet spin state of the (BNBN) ring. In the triplet calculation of (BBNN) O_4 , the two NO molecules tore out from the initial

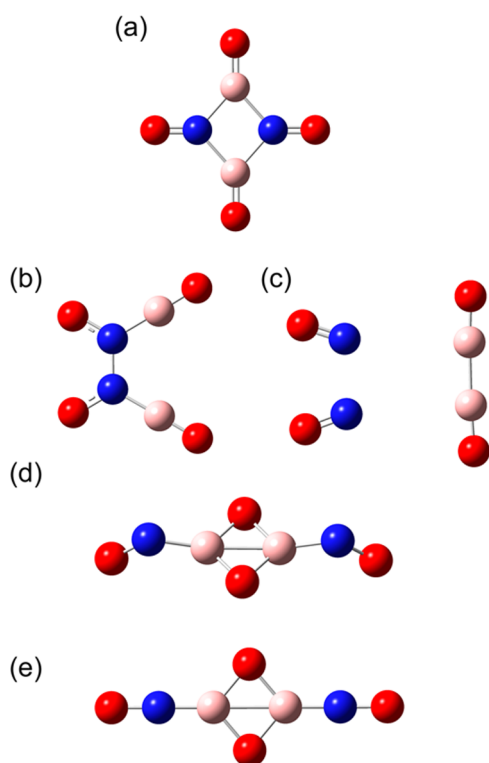
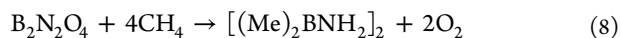


Figure 2. Optimized geometries of isomers of $B_2N_2O_4$ by M06/maug-cc-pVTZ. The names indicate the initial geometries: (a) triplet/singlet $B_2N_2O_4$; (b) singlet $(BBNN)O_4$; (c) triplet $(BBNN)O_4$, in which the structure falls apart; (d) singlet $ON(B_2O_2)NO$; (e) triplet $ON(B_2O_2)NO$.

structure (Figure 2c) and led to the products of reaction 3, which is endothermic by 6.4 kcal/mol. The next tested $B_2N_2O_4$ isomer contains a B_2O_2 ring, and $-NO$ ligands are connected to the boron atoms (see Figure 2d,e). Both the singlet and triplet spin states of $ON(B_2O_2)NO$ are lower in energy by 22.2 and 11.2 kcal/mol, respectively, than the triplet $B_2N_2O_4$ (see Table 3). Also, there are significant structural changes between the triplet and singlet spin states of the $ON(B_2O_2)NO$ isomer. For the triplet structure, the atoms are in a plane (D_{2h} symmetry), and for the singlet structure, the ring slightly bends and the $-NO$ ligands turn out of the plane. Two of these tested isomers, $(BBNN)O_4$ and $ON(B_2O_2)NO$, are lower in energy than triplet $B_2N_2O_4$, but transitions between these isomers require significant structural changes that are expected to lead to large barrier heights. As for the reaction paths leading to the smaller molecules, to get the more stable isomers from the structure of $B_2N_2O_4$, at least two B–N bonds must be broken.

Next, energy differences between the triplet $B_2N_2O_4$ and known and already synthesized $(BN)_2$ ring compounds were calculated. For this purpose, both sides of the equations were extended to get isoelectronic systems. Among the 1,3,2,4-diazadiboretidine derivatives, the $[(Me)_2BNH_2]_2$ molecule was selected as one of the examples, and we found that



is endothermic (35.6 kcal/mol). A similar energy comparison of $B_2N_2O_4$ with a $B_2N_2H_4$ derivative



also gives an endothermic reaction (38.1 kcal/mol).

We conclude that if the $(BNBN)$ ring of $B_2N_2O_4$ is formed, the structure may remain intact for some time.

Electron Distribution in $(CO)_4$ -Like Structures. Analysis of the partial atomic charges and spin densities was carried out for several structures (see Table 4) to find a connection

Table 4. CMS Partial Charges and Hirshfeld Spin Densities for Triplet Spin States of Selected Molecules by M06/maug-cc-pVTZ

molecule	atom ^a	partial charge	$n_\alpha - n_\beta$
$(CO)_4$	C	0.21	0.17
	O	−0.21	0.33
$(SiO)_4$	Si	0.39	0.30
	O	−0.39	0.20
$(CS)_4$	C	−0.01	0.05
	S	0.01	0.45
$(CH)_4$	C	−0.10	0.47
	H	0.10	0.03
$B_2N_2O_4$	B	0.33	0.04
	N	0.01	0.26
	O(B)	−0.39	0.27
	O(N)	0.05	0.43

^aIn parentheses, the connected ring atom is shown if it is necessary for distinction.

between the electron distribution and stability of the triplet state. We note that, for several tested molecules, all three singlet spin states give partial atomic charges very similar to those in the triplet spin states of the same molecules. Therefore, the electron distributions can be understood by examining the triplet states, which is convenient because the atomic spin densities are zero for closed-shell singlets, and the analysis below is carried out that way.

In the $(CO)_4$ molecule, the carbon atoms have cationic character with partial charges of about 0.2. This is quite reasonable when considering the electronegativity difference of carbon (2.55) and oxygen (3.44) atoms. The distribution of partial atomic spin density between the ring atoms (0.17 per carbon) and exocyclic atoms (0.33 per oxygen) is more interesting. In the two singly occupied MOs, the p orbitals of the ring atoms are delocalized (see Figure 1), while the orbitals from oxygen remain localized on the oxygen atoms because the distance between the oxygen atoms is too large (3.22 Å). The major part of the singly occupied electrons is in the localized regions of the MOs. Next we consider this localization/delocalization situation in other cases.

Two molecules, $(SiO)_4$ and $(CS)_4$, that previous work^{3,5} showed to have singlet ground states were investigated in this study to reveal their charge distribution difference from the $(CO)_4$ case. The calculations on $(SiO)_4$ show that the cationic character of silicon atoms is quite large, which is reasonable because silicon has a smaller electronegativity (1.9) than carbon (2.55). Furthermore, the partial atomic spin densities on the silicon atoms are larger than those on the oxygen atoms. Most likely, this phenomenon is related to the metalloid character of the silicon atoms. For the $(CS)_4$ molecule, partial atomic charges are negligible because of the almost equal electronegativity of sulfur (2.58) and carbon (2.55); the main portion (0.45) of the partial atomic spin density is located on each sulfur atom. As a third example, where the triplet spin state fails to be the ground state, cyclobutadiene is also studied. Here the

carbon atoms show anionic character, and the unpaired electrons are almost entirely located on the carbon atoms. In summary, when the partial charge of the ring unit remains neutral, as in $(\text{CS})_4$, or has an anionic character, as in $(\text{CH})_4$, then the closed-shell singlet spin state is preferred. Also, for these molecules, the partial spin density is not shared between the atoms of the ring and ligands; it is to a large extent located only on one of these two subsets of atoms. For $(\text{CS})_4$, those parts of the singly occupied MOs that belong to the carbon ring remain almost empty, and this puts the spin densities on the sulfur atoms. However, in the case of σ -type singly occupied MO (see MO 44 in Figure 1), the S–S distance (3.77 Å) is short enough for overlapping of the orbitals of the sulfur atoms. This leads to an outer delocalized ring, which is energetically preferred over the π -type MO, as was mentioned earlier. Eventually this property leads to the singlet ground state, where this σ -type MO is the HOMO.

In the case of $(\text{SiO})_4$, the silicon ring has twice as large a positive partial atomic charge as the carbon atoms in $(\text{CO})_4$, and a larger portion of the spin density (0.30) is located on each silicon atom, while only 0.17 is located on each carbon atom in $(\text{CO})_4$. Although the planar molecular arrangement of $(\text{SiO})_4$ has a triplet ground state, the true ground state of the $(\text{SiO})_4$ molecule has a tetrahedral geometry and a singlet spin state.

Although the partial charges on boron (0.33) and nitrogen (0.01) differ greatly, their average charge (0.17), when one considers them as BN units, agrees well with the charge (0.21) of the carbon atoms in $(\text{CO})_4$. The partial atomic spin density shows a similar trend; averaging the values for the boron and nitrogen atoms (0.04 and 0.26) gives 0.15, again similar to that of the carbon atoms in $(\text{CO})_4$. This average partial spin density of the BN unit implies that the two unpaired electrons are located primarily (70%) on the exocyclic oxygen atoms with an average unpaired spin of 0.35 units on each oxygen atom.

On the basis of these observations, we deduce the following simple generalizations for analogue molecules of $(\text{CO})_4$ with triplet ground states: (1) The average of the partial charges of the ring atoms in the triplet state should be around +0.2 electrons, and (2) most (about two-thirds) of the spin density in the triplet state should be located on the ligands (as opposed to the ring atoms).

SUMMARY AND CONCLUSION

We have predicted that the $\text{B}_2\text{N}_2\text{O}_4$ molecule has a triplet ground state similar to that of $(\text{CO})_4$. This prediction fits well with what is known about $(\text{BN})_2$ -ring-based C_4 -ring analogues, but an experimental confirmation would be welcome if the molecule or an appropriate precursor molecule can be successfully synthesized. Similar to $(\text{CO})_4$, the $\text{B}_2\text{N}_2\text{O}_4$ molecule is thermodynamically not stable, although kinetic stability might be possible. The propensity for a triplet ground state was discussed in terms of partial atomic charges and spin densities, and the results show that the main part of unpaired electrons are shared among the four exocyclic oxygen atoms. Therefore, they belong to the diradicals but do not show biradical character, where the two radical centers are nearly independent.

The correct energy order for the low-lying electronic states is provided by expensive coupled-cluster calculations, and the much more cost-efficient density functional theory (DFT) calculations give reasonably good (but not entirely correct) predictions for the energies of the low-lying energy states.

COMPUTATIONAL DETAILS

In the DFT calculations of the three singlet $(\text{CO})_4$ analogues, to get all three (π^8 , π^9 , and π^{10}) low-lying electronic states, we first carried out a test calculation, and its MOs were visualized to allow the calculated state to be identified. In subsequent calculations, that configuration was used as an initial guess, and the orbital occupancies were altered to get the rest of the states. After the calculations, the MOs were visualized again to be sure that each calculation provided the desired state.

For open-shell singlet spin states, the Kohn–Sham density functional theory methods do not give pure spin eigenfunctions; the variationally optimized Slater determinants correspond to a significant (or even large) admixture of multiple spin states. For singlet diradicals like $(\text{CO})_4^{5c}$, the usual value of $\langle S^2 \rangle$ is around 1.0. Nevertheless, the Kohn–Sham theory sometimes works well for open-shell singlet spin states, as was shown in several cases in the literature; see, for example, in ref 27 and references cited therein; however, the accuracy is strongly dependent on the choice of the approximate density functional theory and on the system.² To improve the performance of our DFT calculations, we used the method of Yamaguchi, in which one takes a weighted average of the energies of various spin states, with weights determined by the calculated value of $\langle S^2 \rangle$ for the contaminated state.²⁸ In particular, the weighted-average broken-symmetry method²⁸ was applied to the π^9 open-shell singlet spin states; this yields

$$E_S^{\text{sp}} = E_S + \chi(E_S - E_T)$$

$$\chi = (\langle S_S^2 \rangle / \langle S_T^2 \rangle) / [1 - (\langle S_S^2 \rangle / \langle S_T^2 \rangle)]$$

where E_D and $\langle S_D^2 \rangle$ correspond to the total energy and the expectation value of total spin angular momentum for spin state D [where D = singlet (S) or triplet (T)]. The calculations show that there are only small deviations of $\langle S_D^2 \rangle$ values from 1.0 and 2.0 for singlet and triplet states, respectively.

In the CCSD(T) calculations by *Molpro*, to get both of the closed-shell singlet states, the high symmetry of the molecules was exploited. Because the required σ and π orbitals belong to different irreducible representations, the wave functions were constrained as necessary. In the calculation of π^8 and π^9 singlet states by *Gaussian 09*, we applied the same procedure as that in the DFT calculation (see the first paragraph in this section). As mentioned above, unrestricted Hartree–Fock theory is not adequate to describe open-shell singlet states, but if dynamic correlation energy is included in subsequent steps, the effect of the spin contamination becomes less problematic and, as was shown earlier, coupled-cluster methods can perform well in some such cases.^{27,29}

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01223.

Comparison of the molecular geometries of $(\text{CO})_4$ and $\text{B}_2\text{N}_2\text{O}_4$ by CCSD(T)-F12b/cc-pVTZ-F12 (Table S1), Wiberg bond index matrices of triplet $(\text{CO})_4$ and $\text{N}_2\text{B}_2\text{O}_4$ molecules by M06/cc-pVTZ (Table S2), scaled harmonic vibrational frequencies and their IR intensities and Raman activities of the singlet and triplet $\text{B}_2\text{N}_2\text{O}_4$ molecules by M06/maug-cc-pVTZ (Table S3), calculations of $(-\text{CCBN}-)\text{O}_4$ and $(-\text{CCBN})\text{O}_4$ molecules, atomization energy of each molecule in Table 3 calculated by M06/maug-cc-pVTZ (Table S4), Cartesian coordinates (in angstroms) and absolute energies (in hartrees) of calculated structures by M06/cc-pVTZ, of calculated $(\text{CO})_4$ and $\text{B}_2\text{N}_2\text{O}_4$ structures by CCSD(T)/maug-cc-pVTZ, and of calculated $(\text{CO})_4$ and $\text{B}_2\text{N}_2\text{O}_4$ structures by CCSD(T)-F12b/cc-pVTZ-F12 (Tables

S5–S7), extension of Figure 1 to include all MOs (Figure S1), calculated electron affinities and ionization energies of B₂N₂O₄ by M06/maug-cc-pVTZ (Table S8), relative energies, CMS partial charges, and Hirshfeld spin densities for low-energy states of selected molecules by M06/maug-cc-pVTZ (Table S9), and CASSCF and MRCI multireference calculations (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: zvarga@umn.edu.

*E-mail: truhlar@umn.edu.

Notes

The authors declare no competing financial interest.

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