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Why Are S_nN_4 (n = 1−4) Species "Missing"? Answers in a Broader Theoretical Context of Binary S−N Compounds

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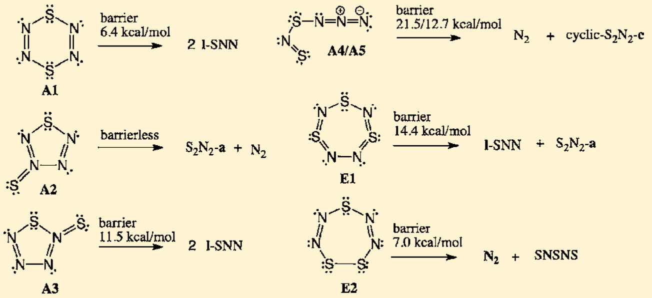
Ⓢ *Supporting Information*

ABSTRACT: Computational investigations of the thermochemical stability and kinetic persistence of binary S_xN_y compounds, SN_2, S_2N_2, S_3N_2, S_4N_2, SN_4, S_2N_4, S_3N_4, and S_4N_4, explain why some S_xN_y stoichiometries exist but not others. There is no direct link between the Hückel 4n + 2 π-electron count rule and the computed heats of formation (per atom) of the lowest-energy neutral S_nN_4 (n = 1−4) isomers, but kinetic persistence often is paramount. Thus, the five lowest-energy S_2N_4 minima at the B3LYP/6-311+G(3df) density functional theory level (**A1−A5**) all not only have high computed heats of formation [$\Delta_fH°(0\ K) > 131$ kcal/mol or >22 kcal/mol/atom] but also have low dissociation barriers (less than 21.5 kcal/mol for the most favorable pathways). For comparison, the persistent (but potentially explosive!) cyclic S_2N_2-**c** has about the same high heat of formation (per atom) as the least unfavorable S_2N_4 isomer, but its barrier to ring opening (51 kcal/mol) is much higher. Although aromatic, both SN_4 (6π electron) and S_3N_4 (10π electron) have low dissociation barriers and, like S_2N_4, are also absent from the S−N binary family.



■ INTRODUCTION

Binary S−N compounds have been known since 1835, when Gregory discovered S_4N_4 by reacting NH_3 with sulfur dichloride.[1] This family, which now includes S_2N_2,[2−4] $S_2N_3^+$,[5] S_3N^-,[6] $S_3N_2^{2+}$,[7] $S_3N_2^{\bullet+}$,[7−9] (also known as loosely bound 14π-electron dimers), $S_3N_3^-$,[10,11] S_4N^-,[12] S_4N_2,[13] $S_4N_3^+$,[14] $S_4N_4^{2+}$,[15] $S_4N_5^+$,[16] $S_4N_5^-$,[17] $S_5N_5^+$,[18,19] and $S_5N_6^+$,[20] has been reviewed comprehensively.[21−23] Except for S_4N_4 and S_4N_2, all have essentially planar geometries. These cyclothiazenes are considered to be "electron-rich" because their π-electron counts exceed the number of ring atoms (each N atom contributes one and each S atom two π electrons). However, "extra" π electrons can be accommodated in relatively low-lying π* orbitals.

In view of the diversity of these cyclothiazenes, some plausible stoichiometries are conspicuous by their absence. Curiously, no SN_4, S_2N_4, or S_3N_4 species, neutral or charged, is known among the many members of the binary S−N family. Is kinetic and/or energetic instability responsible? Answers are explored in the present paper, within the larger context of analyses of the energies, bonding, and decomposition reactions of S−N compounds in general.

Banister[24] was the first to relate the thermochemical stability of S_2N_2 (6π electrons), $S_4N_3^+$ (10π electrons), and $S_5N_5^+$ (14π electrons) to their 4n + 2 π-electron counts. Gimarc and coworkers[25] and Gleiter[26] also noted later that most of these planar heterocycles, although fully inorganic, followed the Hückel aromaticity rule and illustrated the relationship of delocalized π bonding with thermodynamic stability.[27−29] Jung et al.'s study of the S_2N_2 four-membered ring,[30] DeProft et al.'s[31] and Fowler et al.'s[32] investigations of the ring currents of these heterocyclothiazenes, and our recent paper on $S_2N_3^+$[33] are among the more recent theoretical developments. Comparisons of the "aromaticity" or the overall thermodynamic stability of such a diverse set of cations, anions, and neutral species obviously are complicated and have not been attempted. However, we note that kinetic persistence can be even more important. Thus, magnetic criteria indicate that D_{6h} N_6 is just as aromatic as D_{6h} benzene,[34] but N_6 is not viable because it can dissociate readily (low barrier) into three much more stable N_2 fragments.

On the basis of Hückel considerations, the unknown monocyclic SN_4 and S_3N_4 species (6π and 10π electrons, respectively) are expected to be aromatic (we consider them below), but planar S_2N_4 (8π electrons) should be antiaromatic. However, many acyclic and cyclic S_2N_4 isomers are possible; are there any viable preparative candidates among them? Although first- and second-row species are often quite different, the O_2N_4 congener is known experimentally to have an acyclic (bent) structure.[35−38] Six-membered-ring S_2N_4 isomers with 1,2-, 1,3-, and 1,4-sulfur placements are possible. Despite having 8π electrons, puckering might ameliorate their antiaromaticity.

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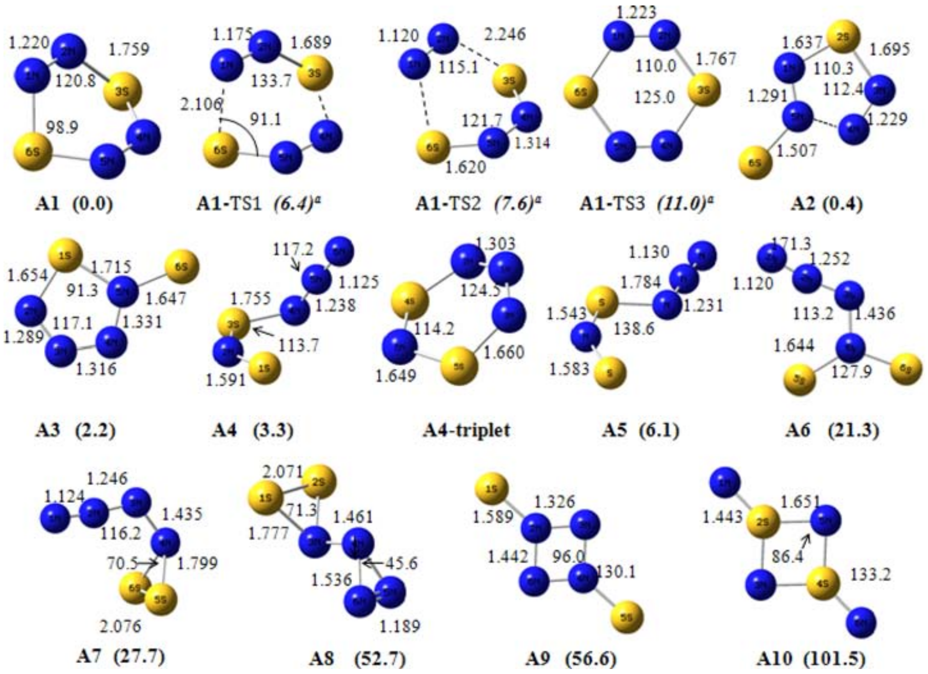

Figure 1. B3LYP/6-311+G(3df) geometries for S_2N_4 isomers. The relative energies (in kcal/mol) of **A2**-**A10**, compared to **A1**, were computed at CCSD(T)/6-311+G(3df)//MP2/6-311+G(3df). ^{a}The relative energies (in kcal/mol) of **A1**-TS1, **A1**-TS2, and **A1**-TS3 compared to **A1**, were computed at B3LYP/6-311+G(3df).

Five-membered-ring S_2N_4 isomers based on parent SN_4 rings have 6π electrons and could be aromatic. Can the family of known S−N compounds be enlarged with S_2N_4 members?

Our extensive exploration of the potential energy surface (PES) of S_2N_4 using stochastic searches (see below) located numerous minima whose structures, energies, and aromaticities were characterized computationally. Examinations of the kinetic stabilities of the lower-energy S_2N_4 isomers were based on the exploration of various possible dissociation channels. Nucleus-independent chemical shifts (NICSs) computations[34,39−46] characterized the magnetic aromaticity of the cyclic S_2N_4 isomers. More broadly, we compare for the first time the relative thermodynamic stabilities of neutral S_nN_4 (n = 1−4) species, including the known lowest-energy isomers of SN_2, S_2N_2, S_3N_2, S_4N_2, and S_4N_4, as well as the unknown SN_4, S_2N_4, and S_3N_4 species. The results are surprising because they do not support the long assumed relationship between the π-electron count (aromaticity) and experimental viability.

COMPUTATIONAL SECTION

All computations were performed at the B3LYP/6-311+G(3df) level,[47,48] as implemented in *Gaussian 03*.[49] Harmonic vibration frequencies computed at the same level established the nature of the stationary points. The performance of this level of theory was compared with the total energies of all S_2N_4 isomers computed at MP2/6-311+G(3df) (including corrections for the zero-point energies scaled by 0.9748[50]) and at CCSD(T)/6-311+G(3df)//MP2/6-311+G(3df). Intrinsic-reaction-coordinate (IRC) scans[51,52] confirmed the identity of the S_2N_4 dissociation products and the isomerization channels. Dissected canonical molecular orbital (CMO) $\mathrm{NICS}(0)_{\pi zz}$[34,41−46] computations at the PW91[53]/IGLO-III[54]//B3LYP/6-311+G(3df) level employed *NBO 5.0*.[55] The most refined NICS index, $\mathrm{NICS}(0)_{\pi zz}$, is based on the out-of-plane tensor components of the isotropic NICS(0), including only the π-orbital contributions. The S_2N_4 isomers located by stochastic "kick" searches[56] at the HF/STO-3G level were reoptimized at B3LYP/6-311+G(3df). The heats of formation for several S_nN_4 (n = 1−4) compounds were computed, at both the B3LYP/6-311+G(3df) and G3B3 levels.[57]

RESULTS AND DISCUSSION

PES Search and Geometries of S_2N_4 Isomers. A total of 10 minima were located on the S_2N_4 PES (see Figure 1). The five thermodynamically most stable species include a six-membered boat-form ring **A1** (1,4-S_2N_4), two five-membered rings (**A2** and **A3**), and two acyclic isomers (**A4** and **A5**; Figure 1). The 8π-electron HCN_3S_2, isoelectronic to **A4**, has a cyclic singlet (C_s) global minimum with a low lying triplet state. Although dithiatriazine dimers, cyclic-$(RCN_3S_2)_2$, have been synthesized, the singlet **A4** adopts and opened form (NNNSNS), and the cyclic triplet C_s minimum is 30.6 kcal/mol higher in energy [at B3LYP/6-311+G(3df)]. Unlike other S−N compounds that favor planar geometries, planar 1,4-S_2N_4 (D_{2h}) **A1**-TS3 is only a transition state (barrier 11.0 kcal/mol) for the interconversion of the boat-form (C_{2v}) minima. This is like the O_2N_4 ring, which favors a boat-shaped six-membered ring, instead of a planar D_{2h} high-energy local minimum.[60] The six-membered 1,2- and 1,3-S_2N_4 rings were not viable; 1,2-S_2N_4 undergoes [2 + 2 + 2] cycloreversion upon optimization and dissociates into S_2 and two N_2 fragments. Planar 1,3-S_2N_4 (C_{2v}) has two imaginary frequencies. Optimization without symmetry constraints led to an acyclic SNSNNN minimum. The other S_2N_4 minima, including one acyclic isomer (**A6**), two three-membered-ring species (**A7** and **A8**), and two four-membered-ring isomers (**A9** and **A10**), are all more than 20 kcal/mol higher in energy (see Table S1 in the Supporting Information) and are not competitive.

The computed energy differences among the five lowest-energy isomers (**A1**−**A5**) are modest [less than 3 kcal/mol with B3LYP and less than 8 kcal/mol for both MP2 and CCSD(T)//MP2], but the stability order varies with the theoretical level. The global minimum of S_2N_4 has not been identified with certainty because different levels of computation

Table 1. Computed $\Delta_f H°$ (at 298 K, in kcal/mol) of S_nN_4 ($n = 1-4$) Isomers at the B3LYP/6-311+G(3df) (the Total Energies Include Thermal Corrections to Enthalpy, in au) and G3B3 Levels

	point group	no. of π electrons	total energies (B3LYP, corrected) in au	$\Delta_f H°$ (B3LYP)^a (per atom) in kcal/mol	total energies (G3B3 enthalpy) in au	$\Delta_f H°$(G3B3)^a (per atom) in kcal/mol
S_8	D_{4d}		−3185.82821		−3184.476973	
N_2	$D_{\infty h}$		−109.558494		−109.484727	
l-SN_2	$C_{\infty v}$		−507.72662	40.9 (13.6)	−507.47576	46.0 (15.3)
S_2N_2 **-b**	C_{2v}	6π	−905.88118	87.6 (21.9)	−905.47079	90.8 (22.7)
S_2N_2 **-c**	D_{2h}	6π	−905.88558	90.3 (22.6)	−905.46882	89.6 (22.4)
S_3N_2 (**B**)	C_{2v}	8π	−1304.10915	93.7 (18.7)	−1303.52639	95.1 (19.0)
S_4N_2 (**C**)	C_s	10π	−1702.34990	89.0 (14.8)	−1701.59822	90.4 (15.0)
SN_4 (**D**)	C_{2v}	6π	−617.18891	101.3 (20.3)	−616.86397	106.6 (21.3)
S_2N_4 (**A1**)	C_{2v}	8π	−1015.37378	131.7 (22.0)	−1014.87657	139.1 (23.2)
S_3N_4 (**E1**)	C_{2v}	10π	−1413.61297	138.1 (19.7)	−1412.94664	151.5 (21.6)
S_3N_4 (**E2**)	C_{2v}	10π	−1413.59684	128.0 (18.3)	−1412.92119	135.6 (19.4)
S_4N_4 (**F**)	D_{2d}	12π	−1811.79873	157.8 (19.7)	−1810.98409	152.5 (19.1)

^{a}The heats of formation for each S_nN_4 ($n = 1-4$) species were computed based on $x[S_8/8] + yN_2$ (x = number of S's, y = number of N_2's) and the experimental $\Delta_f H°$ for N_2 and S_8 (24.02 kcal/mol at 298 K data from the Computational Chemistry Comparison and Benchmark Database, http://cccbdb.nist.gov/).

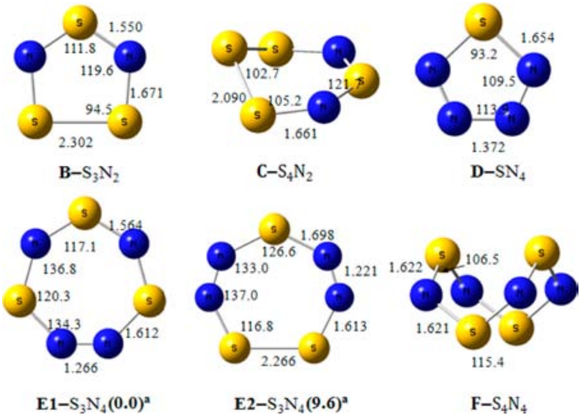

Figure 2. Optimized geometries [at the B3LYP/6-311+G(3df) level] of the S_nN_4 ($n = 1-4$) species. Bond lengths are in angstroms; bond angles are in degrees. ^{a}The relative energies (in kcal/mol) computed at B3LYP/6-311+G(3df) compare two isomers of S_3N_4.

lead to different conclusions [**A4** is the global minimum based on B3LYP/6-311+G(3df), but **A2** is most stable based on the MP2 results].

On the basis of CCSD(T)/6-311+G(3df)//MP2/6-311+G-(3df) single-point energies, **A1** is the global minimum, closely followed by **A2** (0.4 kcal/mol higher in energy) and **A3** (2.2 kcal/mol higher in energy); the highest occupied molecular orbital (HOMO)−lowest unoccupied molecular orbital (LUMO) gaps of **A1** (4.37 eV), **A2** (2.04 eV), and **A3** (1.80 eV) follow the same order. The B3LYP energy order agrees better than MP2, with the more definitive CCSD(T)//MP2 computations. Unlike S_2N_4, the global minimum for O_2N_4 is unambiguous; the best structure is acyclic (bent) and 10−12 kcal/mol (depending on the computational level) more stable than the next preferred five-membered-ring isomer (a ON_4 ring with an exocyclic O−N bond).[37]

Like planar D_{4h} cyclooctatetraene,[61] planar D_{2h} 1,4-S_2N_4 **A1**-TS3 is destabilized (by 11.0 kcal/mol, relative to its C_{2v} boat form) both by angle strain and by its 8π-electron antiaromaticity. Thus, the 8π-electron **A1** (two from each of the N═N double bonds and two from each of the S lone pairs) prefers a puckered geometry. Note the very short N−N bond lengths [1.220 Å, computed at B3LYP/6-311+G(3df); Figure 1] compared to the experimental N═N distance of *trans*-HN═NH (experimental, 1.250 Å; computed, 1.246 Å, at B3LYP/6-311+G**).[62] Divalent sulfur compounds, like their heavier group 16 congeners, prefer bond angles approaching 90°. While the planar D_{2h} S_2N_4 transition state **A1**-TS3 (see Figure 1) has 110° N−S−N angles, ring puckering relieves the angle strain somewhat; the boat-form minimum has 98.9° N−S−N angles. In contrast, **A2** and **A3** have much longer N═N double bonds, shorter S−N single bonds, and smaller N−S−N angles (94.0° and 91.3°; see Figure 1).

Thermochemical Stabilities of the S_nN_4 (n = 1−4) Species. The thermochemical stability of S_2N_4 relative to other neutral S_nN_4 (n = 1−4) species can be evaluated on a common footing by first computing their heats of formation (none appear to have been determined experimentally; see Table 1 and Figure 2) and then comparing their values on a per atom basis. The standard state of elemental sulfur is solid S_8 (the lowest-energy molecular form). The NIST tables give $\Delta_f H°$(gas, 298 K) = +24.02 kcal/mol[63] and nitrogen (N_2) for gas-phase S_8 (Table 1). The computed heats of formation at 298 K, employing the B3LYP/6-311+G(3df) data, are more or less consistent with the G3B3 results listed in Table 1]all data discussed below refer to the B3LYP/6-311+G(3df) $\Delta_f H°$(298 K) results, unless stated otherwise].

Because their computed heats of formation are all positive, the S_nN_4 (n = 1−4) species listed in Table 1 are *unstable* relative to S_8 and N_2. Even the most promising S_2N_4 preparative candidates (**A1** and **A2**) are at least 131.7 kcal/mol higher in energy than $2(S_8/8) + 2N_2$ (see Table 1). Notably, the first experimentally realized S−N compound, S_4N_4, has the highest heat of formation, 157.8 kcal/mol [relative to $4(S_8/8) + 2N_2$; see Table 1]. If it were a planar ring, S_4N_4 would have 12π electrons, but even its puckered minimum is unstable thermodynamically. The energy of the strain-relieving dimerization of the explosive S_2N_2-**c** to give S_4N_4 is only slightly favorable (+22.8 kcal/mol).

Note that all polycyclic aromatic hydrocarbons also have positive heats of formation and thus are thermodynamically

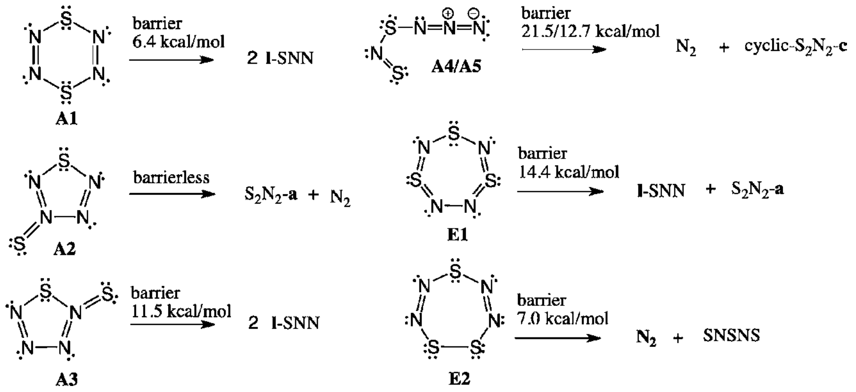

Figure 3. Computed pathways with the lowest dissociation barriers of **A1**−**A5**, **E1**, and **E2** [at B3LYP/6-311+G(3df)].

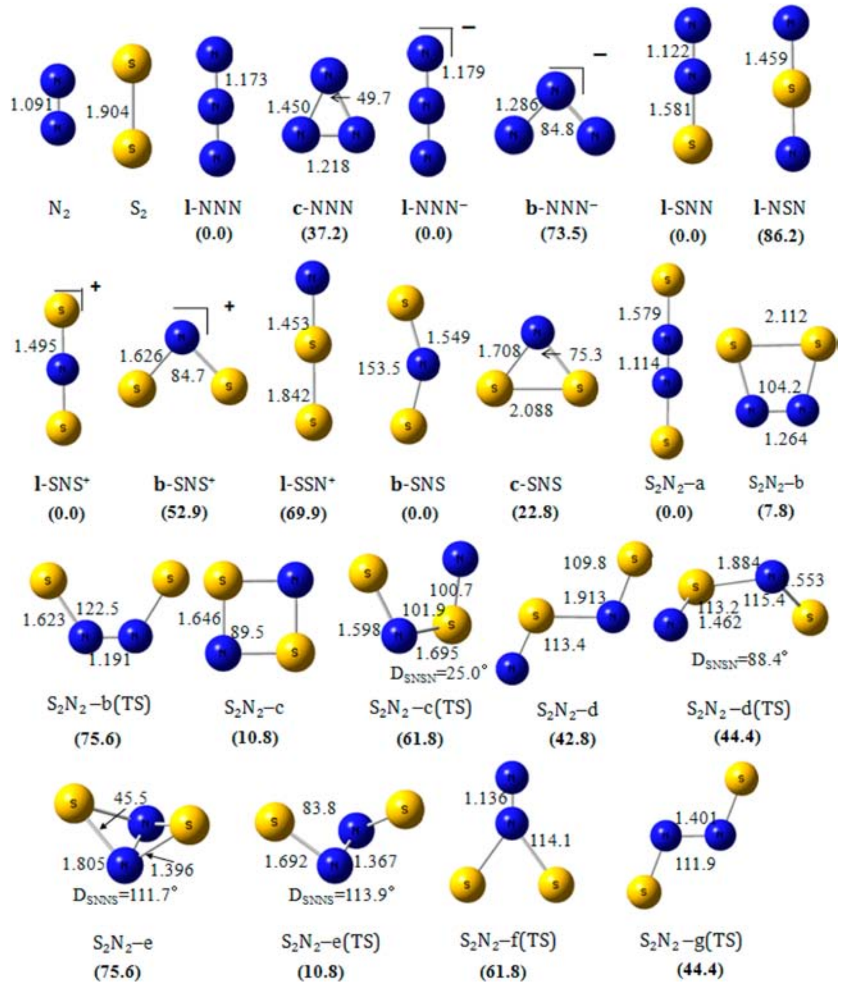

Figure 4. Optimized geometries [at the B3LYP/6-311+G(3df) level] of possible dissociated fragments. Bond lengths are in angstroms; bond angles are in degrees. The energies [at B3LYP/6-311+G(3df), in kcal/mol] of isomers are relative to the corresponding lowest-energy (i.e., the "0.0") structures.

unstable relative to H_2 and graphite. However, the C−C bond energies,[64] e.g., 120.5 kcal/mol for benzene,[64] are much stronger (and less prone to dissociation) than the N−S and S−S bonds in the S_nN_4 (n = 1−4) species. On the basis of their computed atomization energies (G3B3, at 298 K), the S−S bond energy of S_8 (62.5 kcal/mol) and the S−N bond energies of S_4N_4 (70.0 kcal/mol) and S_2N_2-**c** (66.7 kcal/mol) are only about half as strong as the C−C bonds in arenes. Hence, the existence of many of these thermodynamically unstable S−N compounds depends on their kinetic persistence.[33]

On a per atom basis, the heat of formation of the 8π-electron S_2N_4 (**A1**; 22.0 kcal/mol) is essentially the same as the 6π-electron (but strained) S_2N_2-**b** (21.9 kcal/mol) and S_2N_2-**c** (22.6 kcal/mol); the per atom S_4N_4 value (19.7 kcal/mol) is only slightly lower. The 10π-electron S_4N_2 has the lowest heat of formation per atom (14.8 kcal/mol), but otherwise there is no apparent relationship between the aromatic or antiaromatic

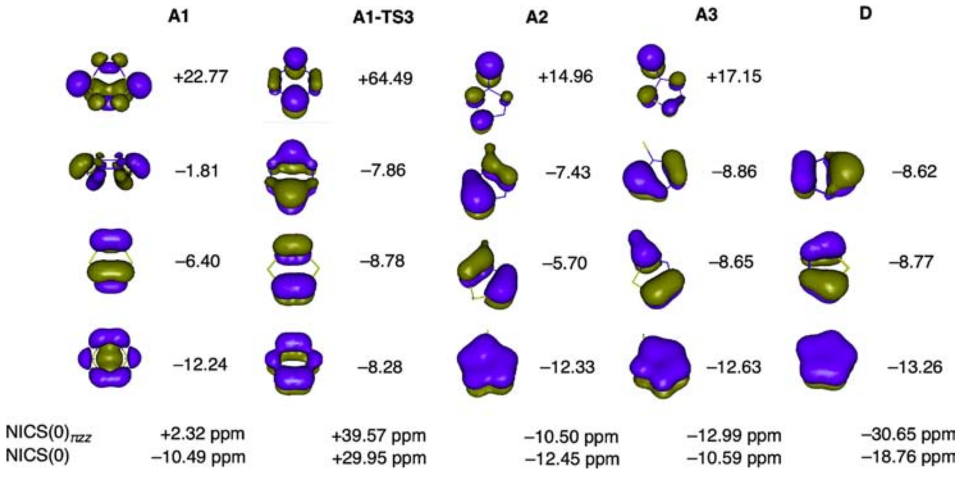

Figure 5. Computed dissected CMO NICS (PW91/IGLOIII) results for cyclic S_2N_4 isomers (**A1**−**A3**), **A1**-TS3, and **D** (SN_4). NICS(0) are isotropic NICS values computed at the ring center. NICS(0)$_{\pi zz}$ are the extracted out-of-plane tensor components of NICS(0), including only the π-orbital contributions.

π-electron counts and the thermodynamic stabilities of the neutral S_nN_4 (n = 1−4) rings. Despite having per atom $\Delta_f H°$(298 K) values close to those of S_4N_4, the 10π-electron S_3N_4, both **E1** (18.3 kcal/mol) and **E2** (19.7 kcal/mol), and the 6π-electron SN_4 (20.3 kcal/mol) have not been realized experimentally because their dissociation barriers are too low (see below).

Dissociation/Isomerization and Kinetic Stability. All cyclic S_2N_4 isomers, other than **A4**, have computed dissociation barriers lower than 13 kcal/mol and thus are not expected to be persistent kinetically except at low temperatures. Both exothermic dissociation pathways of **A1** proceed through cleavage of the long S−N bonds and have small barrier heights: (1) into two l-SNN's (6.4 kcal/mol via **A1**-TS1; see Figure 3) and (2) into N_2 + S_2N_2-**a** (7.6 kcal/mol via **A1**-TS2; see Figures 1 and 4). **A2** also dissociates into two l-SNN fragments through a low barrier (6.2 kcal/mol, via **A2**-TS1 in Figure S1 in the Supporting Information), and the dissociation into N_2 + S_2N_2-**a** through **A2**-TS2 is essentially barrierless [−0.4, or +0.9 kcal/mol based on CCSD(T)/6-311+G(3df)//B3LYP/6-311+G(3df) single-point energies; see Table S2 in the Supporting Information and Figure 3]. In contrast to **A2**, whose rather long N−N bond (1.507 Å; see Figure 1) is responsible for its facile dissociation into N_2 + S_2N_2-**a**, the shorter N−N bond of **A3** (1.316 Å; see Figure 1) results in a somewhat larger (11.5 kcal/mol) activation energy for dissociation of **A3** into two l-SNN fragments (via **A3**-TS1 in Figure S1 in the Supporting Information; see Figure 3). The [3 + 2] cycloreversion of **A3** via **A3**-TS2 has a 19.3 kcal/mol barrier connecting **A6**. The barrier for isomerization in the reverse direction (**A6** to **A3**) is only 1.3 kcal/mol.

The most persistent S_2N_4 isomer, **A4**, is the most likely candidate for experimental observation. Its lowest-energy dissociation into N_2 + S_2N_2-**c** (see Figure 3), via **A4**-TS1 (see Figure S1), is only 21 .5 kcal/mol. However, **A4** is a "floppy" molecule; the **A4**-TS2 (29.7 kcal/mol) and **A4**-TS3 (1.4 kcal/mol) transition states lead to enantiomerization. Other dissociation channels of **A4** are endothermic by 23.8 and 143.9 kcal/mol for l-NNN + b-SNS and l-NNN$^-$ + l-SNS$^+$, respectively. The dissociation of **A5** into N_2 + S_2N_2-**c** through a rather low activation barrier (12.7 kcal/mol, via **A5**-TS in Figure S1 in the Supporting Information; see Figure 3). The dissociation into l-NNN + b-SNS is endothermic by 23.0 kcal/mol.

In addition to its high heat of formation, S_2N_4 is elusive, experimentally, because of the low kinetic persistence of its various isomer. Likewise, the low dissociation barriers of SN_4 to N_2 + N_2S (7.0 kcal/mol),[33] as well as those of the S_3N_4 isomers **E1** to N_2S + SNNS [14.4 kcal/mol, at B3LYP/6-311+G(3df)] and **E2** to N_2 + SNSNS [10.6 kcal/mol, at B3LYP/6-311+G(3df); see Figures 2 and 3], preclude their experimental realization.

Dissociation Fragments. All of the S−N fragments that are likely to result from S_2N_4 dissociation are summarized in Figure 4 (see also Table S3 in the Supporting Information). N_2 and S_2 are the simplest two-atom products. Three-atom products include N_3, SN_2, S_2N, and their ionic forms. Both neutral (l-NNN) and charged (l-NNN$^-$) N−N−N fragments prefer linear structures; their cyclic (c-NNN, with a 49.7° N−N−N angle) and bent (b-NNN$^-$, 84.8° bending angle) isomers are 37.2 and 73.5 kcal/mol higher in energy (see Figure 4). Linear N−S−N (l-NSN) is 86.2 kcal/mol higher in energy than S−N−N (l-SNN) because the N−N bond is stronger than S−N bonds. SNS$^+$ (l-SNS$^+$) has a linear global minimum and is 52.3 kcal/mol lower in energy than the cyclic form (c-SNS$^+$) and 69.3 kcal/mol lower in energy than l-NSS$^+$ (see Figure 4). Neutral S−N−S has a bent global minimum (b-SNS, 153.5° bending angle); the cyclic S−N−S (c-SNS, 75.3° bending angle) is 22.8 kcal/mol higher in energy (see Figure 4).

The four-atom S_2N_2 product has five minima: linear SNNS and cyclic SSNN as well as SNSN, bent SNSN, and "butterfly-shaped" SNSN (see Figure 4). The best known of these, cyclic S_2N_2-**c**, has singlet diradical character[65] (the two N's have negative charges and the positively charged S's each have one π electron with opposite spins) and is 6π aromatic[31,66,67] but is not the thermodynamically most stable S_2N_2 isomer. Instead, S_2N_2-**a** is the S_2N_2 global minimum followed by S_2N_2-**b** and S_2N_2-**c**, which are 7.8 and 10.8 kcal/mol higher in energy, respectively (see Figure 4). The activation energy for the conversion of S_2N_2-**b** into S_2N_2-**a** via S_2N_2-**b**(TS) is 67.8 kcal/mol. Despite its explosive nature, the dissociation of S_2N_2-**c** into two SN molecules, via S_2N_2-**c**(TS), is effectively prohibited by a 50.8 kcal/mol barrier. Neither S_2N_2-**d** nor S_2N_2-**e** is viable; their energies are 42.8 and 57.1 kcal/mol higher than that of S_2N_2-**a**.

Moreover, the activation energy for dissociation of S_2N_2-**d** into two NS molecules, via S_2N_2-**d**(TS), is only 1.6 kcal/mol, and the isomerizarion barrier of S_2N_2-**e** into S_2N_2-**a**, via S_2N_2-**e**(TS), is 4.1 kcal/mol. Both S_2N_2-**f**(TS) and S_2N_2-**g**(TS) are transition states; IRC computations confirm that the reverse and forward products of both are the same. The two mirror-image pathways from C_{2v} transition state S_2N_2-**f**(TS) involve wagging motions and lead to N_2 + S_2, while S_2N_2-**g**(TS) (C_{2h}) follows enantiomeric C_2 pathways, both of which terminate in S_2N_2-**a** ($D_{\infty h}$).

Aromaticity and Antiaromaticity. The magnetic aromaticity of **A1**−**A3**, **A1**-TS3, and **D** (SN_4) are evaluated based on their computed dissected nucleus independent chemical shifts, NICS(0)$_{\pi zz}$, at the ring centers (see Figure 5). NICS(0)$_{\pi zz}$ are the out-of-plane tensor components of the isotropic NICS(0) but include only the π-orbital contributions and are the most refined NICS index.

As expected, the puckered 1,4-S_2N_4, **A1** [NICS(0)$_{\pi zz}$ = +2.3 ppm], exhibits substantially reduced antiaromaticity compared to the planar **A1**-TS3 [NICS(0)$_{\pi zz}$ = +39.6 ppm] and is essentially nonaromatic (see Figure 5). Note that the NICS(0)$_{zz}$ value for the highest π molecular orbital of **A1**-TS3 is highly paratropic (+64.5 ppm), but the corresponding value for **A1** is only +22.8 ppm. Charged 1,4-S_2N_4 isomers, like 1,4-$S_2N_4^{2+}$ and $S_2N_4^{4+}$, could become $4n + 2$ π aromatic. However, 1,4-$S_2N_4^{2+}$ has two imaginary frequencies and, like 1,4-S_2N_4, has 8 (instead of 6) π electrons because the HOMO is a σ ($4b_{1g}$) orbital rather than π ($4b_{1u}$). The two imaginary frequencies, b_{3g} and b_{2u}, are dissociation modes, which lead to two SNN and N_2 + $SNNS^{2+}$, respectively. Although $S_2N_4^{4+}$ has 6π electrons, it has an unrealistic charge and two imaginary frequencies leading to dissociation. Both five-membered-ring S_2N_4 isomers, **A2** [NICS(0)$_{\pi zz}$ = −10.5 ppm] and **A3** [NICS(0)$_{\pi zz}$ = −13.0 ppm], have 6π electrons and are aromatic. The exocyclic S atom reduces the ring aromaticity of both moderately; the parent SN_4 ring has a more negative NICS(0)$_{\pi zz}$ value (−33.0 ppm). Note also that the individual NICS(0)$_{zz}$ contributions of the three lower π molecular orbitals of **A2** and **A3** correspond to those of **A1**-TS3 and SN_4.

Although both **A2** and **A3** are moderately aromatic and **A1** is nonaromatic magnetically, this is not in line with the **A1** > **A2** > **A3** order of their computed total energies at both the CCSD(T)/6-311+G(3df)//MP2/6-311+G(3df) and B3LYP/6-311+G(3df) levels. Clearly, the more aromatic isomers are not always thermodynamically more stable.

■ CONCLUSIONS

Both the energetic instability and the lack of kinetic persistence contribute to the absence of SN_4, S_2N_4, and S_3N_4 species from the binary S−N family. The thermochemical stabilities of the five lowest-energy S_2N_4 isomers (**A1**−**A5**) are quite similar, but the global energy minimum has not been established conclusively because the order is different at the various computational levels. Nevertheless, **A1**−**A5** all have high positive heats of formation (greater than 131 kcal/mol). Like the cyclic $4n$ π-electron D_{2d} cyclooctatetraene, 1,4-S_2N_4 (**A1**) prefers a puckered geometry and is essentially nonaromatic. Kinetically, **A1**, as well as the moderately aromatic **A1**, have low dissociation barriers and thus are likely to be persistent. **A3** and **A5** have dissociation barriers of less than 13 kcal/mol and are only expected to have fleeting lifetimes. **A4** appears to be the best possible S_2N_4 preparative candidate, but its dissociation barrier (resulting in N_2 + S_2N_2-**c**) is only 21.6 kcal/mol. Both cyclic S_2N_2 forms (S_2N_2-**b** and S_2N_2-**c**) have essentially the same heats of formation per atom as that of S_2N_4 but have high barriers (more 50 kcal/mol) to ring opening. The experimental realization of binary S−N compounds often depends more on their kinetic persistence rather than their thermodynamic stability. The computed heats of formation of these binary S_nN_4 (n = 1−4) compounds also do not follow the expected thermodynamic stabilities based on the Hückel $4n + 2$ π-electron aromaticity rule.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Total energies, unscaled zero-point energies, relative energies, computed $\Delta_f H°(0\ K)$, and optimized transition structures of **A2**−**A5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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