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Article

Lowest Singlet and Triplet Potential Energy Surfaces of S_2N_2

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Forty four stationary points have been located on the lowest singlet and triplet potential energy surfaces of S_2N_2. Ten minima and ten saddle points on the lowest singlet surface and eleven minima and thirteen saddle points on the lowest triplet surface were found. All saddle points were connected to minima or lower-order saddle points by following the intrinsic reaction coordinate. Renner–Teller effects in the linear isomers were studied by examining their bending curves. The S_2N_2 polymerization mechanism was investigated by first locating the transition state corresponding to ring opening and then considering all species connected to it that are close in energy. The commonly accepted mechanism is problematic due to the number of species that would lead to dissociation to SN + SN. Other possible isomers that are consistent with the experimental evidence but do not connect to SN radicals in the dissociation limit were examined. A mechanism of polymerization to $(SN)_x$ is proposed that involves excitation of the square planar singlet molecule to the triplet surface. The triplet species then undergoes a puckering, and polymerization occurs in a direction approximately perpendicular to the S_2N_2 plane. Consideration of the predicted vibrational frequencies suggests the structure of the second isomer of S_2N_2. This isomer has a *trans*-NSSN structure with a long SS bond. The energetics of *trans*-NSSN are consistent with the observed temperature effects in the dimerization of SN. Analysis of the bending curves of linear NSSN and NSNS indicates that *trans*-NSSN is the only isomer which has a small yet significant barrier to that dimerization.

1. Introduction

Disulfur dinitride, S_2N_2, has been the focus of many studies. The first reported synthesis was in 1953 when Goehring and Voigt obtained S_2N_2 by heating S_4N_4 to a temperature of 300 °C, passing the subsequent vapor through silver wool, and sublimating it on a coldfinger.[1] In 1966, the IR spectrum was obtained[2] and the pattern of peaks correlated with a planar alternating ring structure of D_{2h} symmetry. This conclusion was later confirmed by X-ray crystallography.[3] This structure and its bonding are rather extraordinary, and the electronic nature of S_2N_2 has been the topic of many ongoing discussions and has received renewed attention.[4,5]

Crystals of S_2N_2 polymerize in the solid state. The resulting compound, $(SN)_x$, has a metallic conductivity and, at low temperatures, is superconducting.[6] This material has been incorporated into electronic devices. The mechanism for this polymerization has been extensively studied and is thought to involve a radical intermediate, as shown by electron spin resonance (ESR) studies,[7] and to require an activation energy of 41 kcal/mol.[6] Vaporization of $(SN)_x$ leads to a number of products,[8,9] including the precursor S_2N_2,[10] and this behavior is not typical of a polymer. A more recent article examined the solid-state polymerization process[11] using X-ray diffraction techniques and supported the previous supposition of a

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least-motion mechanism.[6] This proposal does not, however, account for the products observed upon vaporization and their subsequent reaction to regenerate $(SN)_x$.[9]

Theoretical methods have been used previously to examine the conversion of S_2N_2 to $(SN)_x$. Palmer and Guest studied the electronically excited states of S_2N_2 to identify the radical intermediate in the polymerization mechanism.[12] Their findings confirmed the existence of a number of low-lying triplet excited states that could take part in the polymerization process. However, their calculations were limited to the triplet state at only two geometries, a closed D_{2h} structure like S_2N_2 and an open C_s structure corresponding to the geometry of a single SNSN subunit in $(SN)_x$. They did not examine any other possible intermediates. In fact, to our knowledge, no detailed theoretical study of the mechanism of polymerization or any extensive mapping of the triplet surface of S_2N_2 has been published.

In 1992, Hassanzadeh and Andrews reported the observation of an IR band, appearing in conjunction with diatomic SN in an argon matrix, which they attributed to a new isomer of S_2N_2.[13] This, in turn, fueled the first extensive exploration of the S_2N_2 singlet potential energy surface.[14] Using wave function based methods, Warren et al. concluded, based on vibrational frequency predictions, that the S_2N_2 species observed in the argon matrix was the previously unobserved planar pairwise ring. Shortly thereafter, density functional theory (DFT) studies refuted this claim.[15] However, these DFT studies were limited to only a few structures and did not comment further on the identity of the second isomer.

In this work, fairly extensive mappings of both the lowest singlet and lowest triplet potential energy surfaces of S_2N_2 are presented. These results will be used to examine the mechanism of polymerization to $(SN)_x$, with additional reference to experiment, to assess the structure of the second isomer of S_2N_2 and its formation, and to examine if other isomers can be similarly formed.

2. Computational Methods

The computational package employed was Gaussian98.[16] The geometries of all species were optimized and their vibrational spectra characterized using the Becke 3 parameter exchange functional (B3)[17] and the Lee, Yang, and Parr correlation functional (LYP).[18,19] The effective core potential basis set of Stevens, Basch, and Krauss[20] was used, and sets of d-type polarization functions[21] were added to both S and N.[22] This combination of method and basis set was shown to be a suitable compromise between performance and computational efficiency[23] for a wide range of compounds containing sulfur and nitrogen.

All bond lengths are reported in angstroms, angles in degrees, and relative energies, which include the zero-point vibrational energy corrections, in kcal/mol. Frequencies are reported in cm^{-1} and the infrared intensities in km/mol. The imaginary frequencies of transition states were followed using the Intrinsic Reaction Coordinate (IRC) method.[24]

3. Results and Discussion

3.A. Formation and Dissociation of S_2N_2. The well-known square planar species in the solid state is a concussive explosive,[25] corresponding to a metastable system. The second isomer of S_2N_2 has only been observed in matrix isolation experiments where it is formed in a nitrogen−sulfur−argon discharge.[13] An examination of the channels of formation and dissociation of S_2N_2 may provide further insight into the metastability of this molecule. Also, an assessment of the chosen theoretical model for predicting these smaller systems, relative to experiment or earlier predictions, will demonstrate its inherent errors. Results on atomic, diatomic, and triatomic nitrogen and sulfur species along with the energetic ordering of selected dissociation channels are given in Table 1.

The difference between the ground state ^4S and first excited ^2D energies of atomic nitrogen is 55.0 kcal/mol.[26] The energy difference from the present theoretical model is too large by 8.8 kcal/mol or 16%. The first excited state of the sulfur atom, ^1D, lies 26.4 kcal/mol above the ground electronic state ^3P.[26] A ^1D atomic state cannot be correctly described with a single determinant, and the closed-shell method predicts the energy difference for a singlet sulfur atom to be 40.1 kcal/mol.

One method for examining open-shell systems is to use an unrestricted broken symmetry approximation in which the highest-occupied and lowest-unoccupied orbitals are mixed to crudely model an open-shell singlet. This leads to a predicted energy difference of only 8.4 kcal/mol. An alternative method for describing an open shell system is to use complex orbitals. The implementation of this method in Gaussian98, however, is limited to Hartree−Fock and second-order Møller−Plesset (MP2). To remain consistent yet resolve this issue, the MP2 implementation was chosen

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so as to include electron correlation. Single point MP2 energy calculations were performed, both with and without the use of complex orbitals, to assess the energy difference between the closed- and open-shell species. This energy difference, 13.7 kcal/mol, was used to correct the closed-shell B3LYP energy difference of 40.1 kcal/mol, resulting in a predicted separation of 26.4 kcal/mol between ^3P and ^1D. This procedure allows corrections to the energies of the channels for dissociation to atoms.

Diatomic nitrogen, N_2, has a $X^1\Sigma_g^+$ ground state. The first excited electronic state, $a^3\Sigma_u^+$, is higher in energy by 143.5 kcal/mo,l[27] and thus the predicted energy difference is 13.5 kcal/mol or 9% larger. The predicted bond distances for the two states, 1.132 and 1.303 Å, are both longer than the experimentally reported values of 1.098 and 1.293 Å.[27] This overestimation of bond distances is consistent with the previous findings for the present combination of exchange-correlation functional and basis set.[23]

The diatomic sulfur species has a $X^3\Sigma_g^-$ ground electronic state and a first excited electronic state, $a^1\Delta_g$, lying 13.4 kcal/mol higher in energy.[27] As noted for the sulfur atom, a theoretical description of the first excited singlet state is problematic within a single determinant model. A similar correction to that described for the sulfur atom was applied. The energy difference, 6.4 kcal/mol, between the real and complex MP2 solutions for the singlet states at the closed shell bond distance of 1.943 Å was used as a correction to the closed shell B3LYP energy difference. The corrected energy difference of 17.3 kcal/mol, in Table 1, is 3.9 kcal/mol larger than the experimental value.[27] The predicted bond length of 1.942 Å for the ground triplet state is longer than the experimentally observed value of 1.889 Å.[27]

The SN radical has a $X^2\Pi$ ground electronic state. The predicted bond length for this system in Table 1 is longer than the experimentally observed value.[27] The magnitude of the error in the bond length is similar to that noted for the ground electronic state of N_2. There do not appear to be experimental or theoretical results published for the excited $a^4\Sigma^-$ electronic state of SN. We predict this state to lie adiabatically 75.7 kcal/mol above the ground state with a bond distance of 1.623 Å, nearly 0.1 Å longer than that in the $X^2\Pi$ state.

The triatomic systems, S_2N and SN_2, have previously been considered theoretically.[15,28−32] There is only one publication of experimental results, a Fourier transform IR study of the linear NNS molecule.[33] Thus the present findings are mostly compared with earlier theoretical predictions. Results are given in Table 1.

Table 1. Results for Small Molecules Containing Sulfur and Nitrogen and the Dissociation Channels[a]

atom

	electronic state	rel energy
N	^4S	0.0[b] [0.0][c]
	^2D	63.8 [55.0][c]
S	^3P	0.0[b] [0.0][c]
	^1D	26.4[d] [26.4][c]
	^1S	40.1 [- - - -]

diatomic molecules

	electronic state	rel energy	bond length
N_2	$X^1\Sigma_g^+$	0.0[b][0.0][e]	1.132 [1.098][e]
	$a^3\Sigma_u^+$	130.1 [143.5][e]	1.303 [1.293][e]
S_2	$X^3\Sigma_g^-$	0.0[b][0.0][e]	1.942 [1.889][e]
	$a^1\Delta_g$	17.3[d][13.4][e]	- - - - [1.898][e]
	$b^1\Sigma_g^+$	23.7 [- - - -]	1.943 [- - - -]
SN	$X^2\Pi$	0.0[b][0.0][e]	1.527 [1.494][e]
	$a^4\Sigma^-$	75.7 [- - - -]	1.623 [- - - -]

S_2N **triatomic molecules,** SNS $^2A_1$

level of theory	rel energy	r_{SN}	θ_{SNS}
B3LYP/cep-31G*	0.0[b]	1.583	150
CCSD/DZP[f]		1.582	148.0
CISD/TZ2P[g]	0.0	1.546	151.3
MP2/6-311++G(d,p)[h]	0.0	1.555	148.6
B3LYP/TZ2P[i]		1.557	150.9

S_2N **triatomic molecules,** SSN $^2A'$

level of theory	rel energy	r_{SS}	r_{SN}	θ_{SSN}
B3LYP/cep-31G*	22.2	1.983	1.590	115
CISD/TZ2P[g]	19.2 (20.1)[j]	1.921	1.528	116.8
MP2/6-311++G(d,p)[h]	18.6	1.929	1.574	117.0

N_2S triatomic molecules, NNS $^1\Sigma^+$

level of theory	rel energy	r_{NN}	r_{SN}
B3LYP/cep-31G*	0.0[b]	1.161	1.607
CASSCF/DZP[k]	0.0	1.140	1.645
CCSD(T)/cc-pVQZ[l]		1.128	1.590
experiment[m]		1.139	1.578

N_2S triatomic molecules, NSN $^1A_1$

level of theory	rel energy	r_{SN}	r_{NN}	θ_{NSN}
B3LYP/cep-31G*	35.9	1.929	1.193	36
CASSCF/DZP[k]	40.9	2.025	1.172	33.6

N_2S triatomic molecules, NSN $^1\Sigma_g^+$

level of theory	rel energy	r_{SN}
B3LYP/cep-31G*	93.1	1.494
CASSCF/DZP[k]	105.2	1.510

channel	dissociation limits	rel energy
A	S_2 ($X^3\Sigma_g^-$) + N_2 ($X^1\Sigma_g^+$)	0.0
B	S_2 ($a^1\Delta_g$) + N_2 ($X^1\Sigma_g^+$)	17.3
C	NNS ($X^1\Sigma^+$) + S (X^3P)	74.0
D	SN ($X^2\Pi$) + SN ($X^2\Pi$)	94.9
E	NNS ($X^1\Sigma^+$) + S (a^1D)	100.4
F	NSN (A^1A_1) + S (X^3P)	109.9
G	SNS (X^2A_1) + N (X^4S)	133.4
H	NSN (A^1A_1) + S (a^1D)	136.3
I	SSN (A^2A') + N (X^4S)	155.6
atomization	2 S (X^3P) + 2 N (X^4S)	290.0

[a] Relative energies in kcal/mol, distances in angstroms, angles in degrees. [b] B3LYP/cep-31G* energies (in hartree): N = 9.750176, S = 10.064815, N_2 = 19.816654, S_2 = 20.278483, SN = 19.970446, S_2N = 30.129423, N_2S = 29.909442. [d] Corrected using an MP2/cep-31G* complex solution (see text). [c] Reference 26. [e] Reference 27. [f] Reference 28. [g] Reference 29. [h] Reference 30. [i] Reference 15. [j] CISD + Q. [k] Reference 31. [l] Reference 32. [m] Reference 33.

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The lowest energy isomer of S_2N, with two equivalent NS bonds, has a bent structure and a $^2A_1$ electronic state. The predicted bond distance of 1.583 Å and bond angle of 150° are in reasonable agreement with earlier predictions. In particular, the CCSD/DZP NS bond distance of Kaldor[28] is nearly identical to the present result and the bond angle approximately 2° smaller. Other correlated methods employing larger basis sets predicted a bond distance that is ca. 0.03 Å shorter than that from the present method. Thus the present predicted value is almost certainly too long, which is consistent with previous conclusions. For the bond angle, the value is constant to within approximately 2° with theoretical method and basis set.

The SSN isomer is bent with a $^2A'$ electronic state. It is consistently predicted to lie adiabatically 18.6−22.2 kcal/mol above the $^2A_1$ S_2N species. There is greater variation in the predicted structures for SSN. Compared with the earlier MP2 results,[14] a much longer SS distance and only a slightly longer SN bond length are predicted with the present method. On comparison of the present results to a higher level of theory, CISD/TZ2P, the SS and SN bonds are too long by similar amounts, ca. 0.06 Å.[29] The bond angles vary only slightly, ca. 2°, among the different methods.

Three isomers of N_2S were considered: linear NNS, bent NSN, and linear NSN. The most stable isomer is linear NNS. It has a $X^1\Sigma^+$ ground electronic state and the experimentally determined bond distances are 1.139 Å (NN) and 1.578 Å (NS).[33] The earlier complete active space-self consistent field (CASSCF) result[31] is in near perfect agreement with experiment for the NN bond distance, but the SN distance is too long by nearly 0.07 Å. The 1996 coupled-cluster with single and double and perturbative triple excitations (CCSD(T)) result for the NN bond was too short by 0.011 Å, and the SN bond was too long by 0.012 Å.[32] Both higher level methods show an inequivalent treatment of the two bonds. The present method overestimates, to about the same degree, both the NN and NS bond lengths, by 0.022 and 0.029 Å, respectively.

Bent NSN, the next lowest energy isomer, has a $^1A_1$ ground electronic state. The predicted bond angles are 36° (B3LYP/cep-31G*) and 33.6° (CASSCF/DZP) (see Table 1). Despite this very acute angle, the stabilization due to the short (and strong) NN bond causes this ring structure to lie only ca. 40 kcal/mol above linear NNS. The predicted energy difference of 35.9 kcal/mol from this work is slightly smaller than that given by CASSCF.[31] Similar to the linear NNS situation, the predicted NN distance in the present work is slightly longer than the CASSCF result and the NS bond counterintuitively shorter. Given our results on the more stable isomer, as well as those for the other species, the actual SN distance is expected to be approximately 1.90 Å. For the third isomer, linear NSN, the B3LYP/cep-31G* predicted energy difference relative to the NNS species is too small by ca. 15% and the SN bond distance slightly too short compared to the previous CASSCF results. Considering that the CASSCF SN bond distance in linear NNS is 0.07 Å too long, while ours was 0.03 Å too long, it is not surprising that our predicted value atypically appears to be too short. Both methods predict this species to be high in energy.

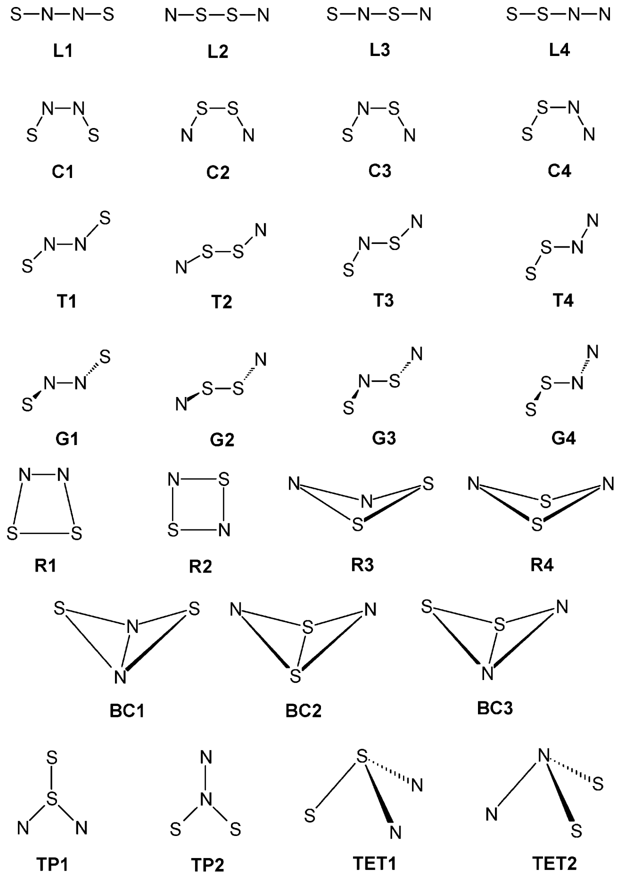
In summary, the B3LYP/cep-31G* method overestimates bond distances by 0.02−0.03 Å, predicts energy differences that are, on average, too large by ca. 5 kcal/mol, and slightly underestimates bond angles by approximately 1°. These trends are consistent.

Ten dissociation channels are listed in Table 1. The lowest channels naturally correlate with the exceptionally stable N_2 molecule and a diatomic sulfur molecule. The energy difference between the two lowest channels is the singlet−triplet energy difference in S_2. These two $S_2 + N_2$ channels therefore can correlate with the ground singlet and lowest excited triplet electronic surfaces, respectively. Both channels also lie in energy below the most stable isomer of S_2N_2. Such an order is consistent with the metastable character of S_2N_2 and the well-known fact that all binary sulfur−nitrogen compounds are explosive. The next highest dissociation channel involves NNS. This channel (NNS + S) also correlates with the lowest singlet and triplet surfaces of S_2N_2 as the sulfur atom may be either ^3P or ^1D. The only channel, below 100 kcal/mol, that correlates simultaneously with both electronic states of S_2N_2 involves the two diatomic radicals, SN + SN. This correlation will be important in the discussion of the formation of new isomers of S_2N_2. The remaining channels, including the atomization channel, lie above 100 kcal/mol.

3.B. S_2N_2. Tetra-atomic binary compounds, such as S_2N_2, could exist in a number of structures: chains, rings, etc. Each structure could have geometric isomers. For example, a chain might exist in linear or bent forms and the latter may be found in cis, trans, or gauche configurations. Likewise, a ring could be planar or puckered and composed of three or four atoms. The potential energy surfaces of such a relatively simple molecule as S_2N_2 could be very complex. In this study, interconversions between various isomers and the relationships to the dissociation channels are examined. The mapping, however, does not attempt to connect all the minima via transition states. To aid in the presentation, the isomers were classified according to their structures as shown in Chart 1.

In the previous section, predictions of the properties for smaller systems were assessed. Since the three lowest isomers of S_2N_2 (L1, R1, and R2; Chart 1) have already been examined thoroughly,[14,15] those results can further confirm the present analysis. The results are collected in Table 2. The predicted bond lengths from this study are typically too long. There are a few exceptions of which the most notable are the BLYP results for SS and SN and the MP2 results for NN. Compared with the other B3LYP results, the present bond distances are again consistently too long. As noted earlier, the present method should predict bond lengths that are too long by ca. 0.02−0.03 Å and the reliability of the BLYP and MP2 predictions of bond lengths for these species comes into some question. As noted by Somasundram and Handy,[15] higher level calculations, such as CASSCF and MRCISD, confirmed the predicted energy orderings from DFT (i.e., L1 < R1 < R2) but not the exact energy

Chart 1. The Isomers of S_2N_2[a]



[a] Key: L = linear, C = cis, T = trans, G = gauche, R = ring, BC = biyclic, TP = trigonal planar, and TET = tetrahedral.

differences. The same L1 to R2 energy difference is predicted here as in the other B3LYP results. The energy of R1 relative to L1 is considerably smaller. The CASSCF difference in energy between R1 and R2 was 6.5 kcal/mol.[15] Overall, the results follow the same pattern observed for the smaller molecules.

The relative energies of each stationary point with respect to the lowest energy isomer, L1, on the singlet surface, are shown in Figures 1 and 2. A few of the dissociation channels have been included. Dashed lines connect saddle points to their corresponding minima or to other saddle points of lower order as determined from the IRCs. The three lowest energy minima (L1, R1, and R2) lie on the singlet potential energy surface. As noted earlier, all isomers of S_2N_2 are less stable than the dissociation channels to disulfur and dinitrogen. The singlet surface channel is 33.8 kcal/mol and the triplet surface channel 51.1 kcal/mol lower in energy. This makes even the most stable S_2N_2 species metastable.

The optimized structure of each point, labeled with the basic structure (Chart 1), electronic state, and highest occupied molecular orbitals (HOMOs), are given in Figures 3−6. The results for isomers corresponding to structure L4 (Chart 1) are not included. Isomers of L4 are artifacts with very long SN bond distances (>4 Å) and small imaginary frequencies ($<20i$ cm^{-1}). The relative energies are very close to those of isolated $S_2 + N_2$.

A number of the isomers on the singlet surface have been characterized previously. In the DFT study, five isomers, L1, C2, R1, R2, and a TP2 variant which has an SNN ring,[15] were studied. With the exception of the LDA and BLYP functionals, the structure C2 either converged to a linear structure (i.e., L2) or dissociated into two SN radicals. This behavior also is observed in the present work. The only isomer that was not found by the present method is the TP2 variant. In another earlier study, a more thorough search was performed.[14] Nine isomers on the singlet surface, L1, C2, T2, T3, R1, R2, BC1, TP1, and the TP2 variant, were located. As already mentioned, the C2 and the TP2 variant were not predicted in the present study. All the other isomers were located as were three previously unobserved species, C1, C3, and TP1−2 (which has an SSN three-member ring). L1, R1, and R2 were discussed above. Comparisons involving the remaining isomers (T2, T3, BC1, and TP1) follow.

The two trans chains, T2 and T3, lie slightly above the SN + SN dissociation channel limit (Figure 1). Warren et al. located these minima only on the HF surface.[14] Searches of the MP2 surface found that *trans*-NSSN, T2, dissociated into SN + SN and *trans*-NSNS, T3, was a transition state. Those results and the present research predict long central bonds for *trans*-NSSN, which imply weakly bound dimers. There is a barrier to dissociation of ca. 12 kcal/mol. If the HF geometry was used as the initial point in the MP2 optimization, it could be on a part of the surface above the barrier. Geometry optimization to this shallow minimum would be difficult, and the dissociated species could be obtained. For the *trans*-NSNS species, T3, the central bond is not as long as that in *trans*-NSSN. Both a minimum and a transition state for *trans*-NSNS were optimized on the singlet surface in the present study. The difference between these two stationary points is traced to different HOMOs. In the minimum, the highest occupied orbital is a′, whereas in the transition state it is a″.

The BC1 isomer is predicted to be nearly isoenergetic with T2. A similar result was observed with HF/6-31G*. The BC1 B3LYP/cep-31G* NN and NS bond distances, 1.407 and 1.841 Å (Figure 3), are comparable to those from MP2/6-31G*, 1.394 and 1.841 Å.[14] The TP1 structure, with predicted SS and SN distances of 1.926 and 1.551 Å (Figure 3), differs from the MP2 results, 1.909 and 1.575 Å, by ca. 0.02 Å. Energetically, the present B3LYP and earlier MP2 results place TP1 ca. 50 kcal/mol above the BC1 isomer.

A number of isomers exist on the singlet and triplet surfaces at energies of 30−90 kcal/mol with respect to L1. The dissociation channel to SN + SN is in this energy range. See Figures 1 and 2. The number of isomers increases the complexity of the chemistry of S_2N_2. Polymerization to $(SN)_x$, the identity of the second isomer of S_2N_2 observed in the matrix isolation experiments, and the possibility of observing other new S_2N_2 isomers all must be considered.

3.C. Polymerization of S_2N_2 to $(SN)_x$. The "classical" route for the synthesis of $(SN)_x$, especially for preparing the polymer in high enough purity for electronic applications, is the solid-state polymerization of S_2N_2.[6] The proposed mechanism for this is a "one-point ring cleavage where the

Table 2. Results for the three lowest isomers (L1, R1, and R2 in Chart 1) of S_2N_2[a]

	L1			R1				R2	
level of theory	r_{NS}	r_{NN}	ΔE	r_{NN}	r_{SS}	r_{SN}	ΔE	r_{SN}	ΔE
B3LYP/cep-31G*	1.607	1.175	0.0[d]	1.281	2.148	1.762	2.1	1.683	12.0
LDA/6-31G*[b]	1.571	1.159	0.0	1.265	2.122	1.738	15.1	1.660	23.5
BLYP/6-31G*[b]	1.603	1.167	0.0	1.269	2.192	1.804	14.9	1.702	27.4
MP2/6-31G*[c]	1.570	1.190	0.0	1.301	2.100	1.723	18.5	1.684	12.3
MP2/6-311G(2df)[c]	1.563	1.161	0.0	1.311	2.072	1.700	12.5	1.669	1.7
MP2/6-311++G(3df)[c]	1.559	1.183	0.0	1.320	2.059	1.689	11.6	1.663	−0.2
BLYP/TZ2P[b]	1.596	1.158	0.0	1.273	2.170	1.775	11.7	1.683	17.0
B3LYP/TZ2P[b]	1.586	1.139	0.0	1.260	2.132	1.737	8.1	1.652	12.8
B3LYP/TZ2P+f[b]	1.580	1.142	0.0	1.264	2.112	1.726	8.3	1.646	11.2

[a] Bond lengths in Å, relative energies in kcal/mol. [b] Reference 15. [c] Reference 14. [d] Total energy (in hartree): −40.003583.

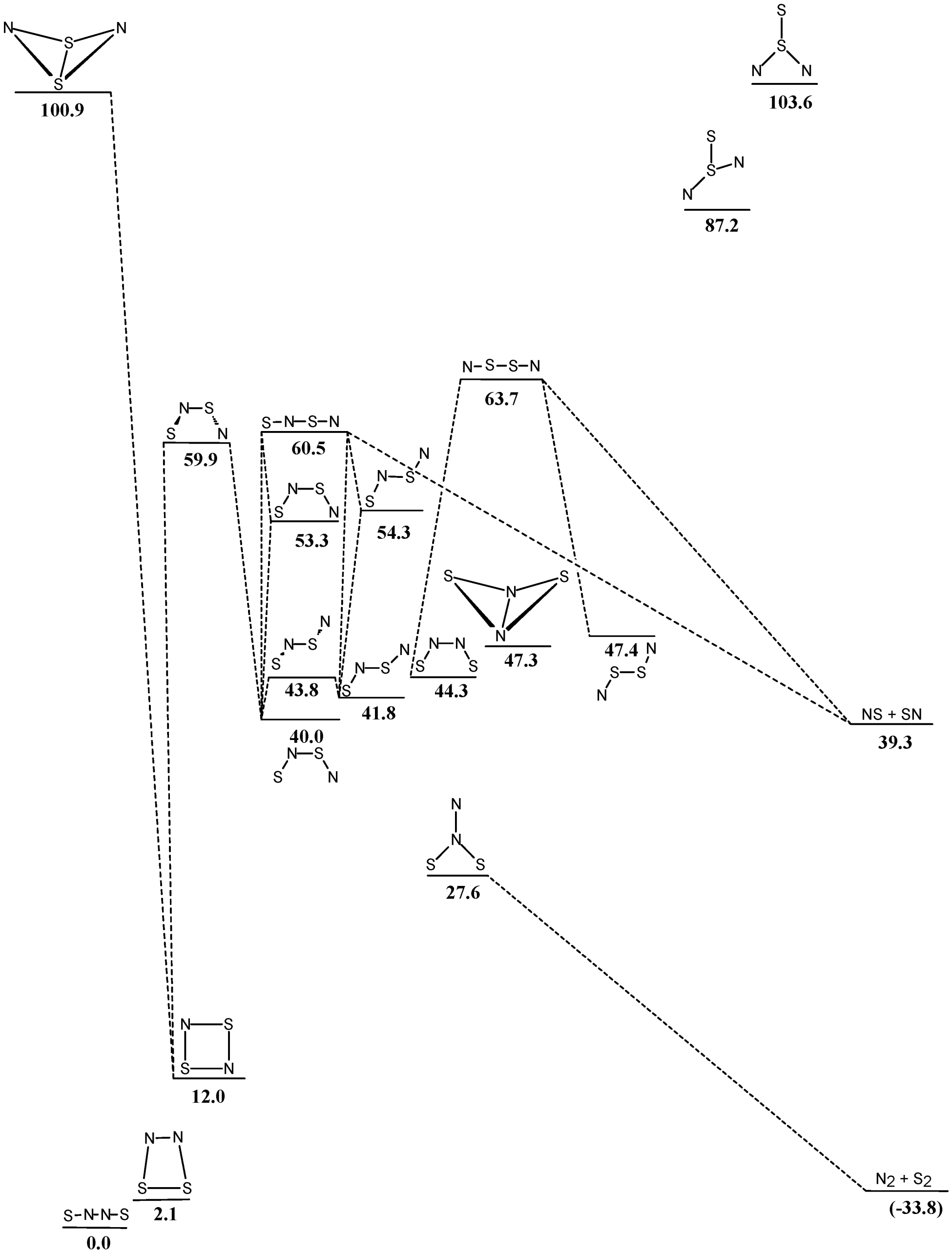


Figure 1. Relative energies (in kcal/mol) of all stationary points on the lowest singlet potential energy surface of S_2N_2.

root-mean-square displacements of the atoms involved are minimized".[6] As shown in Figure 7a, this statement implies that the individual S_2N_2 molecules undergo a ring cleavage forming a cis-chain, similar to C3, and the chains join to form ribbons of $(SN)_x$. This mechanism is consistent with a number of experimental observations, including an activation energy of 41 kcal/mol.[34,35] However, it is inconsistent with the vapor phase studies, where $(SN)_x$ decomposes into a

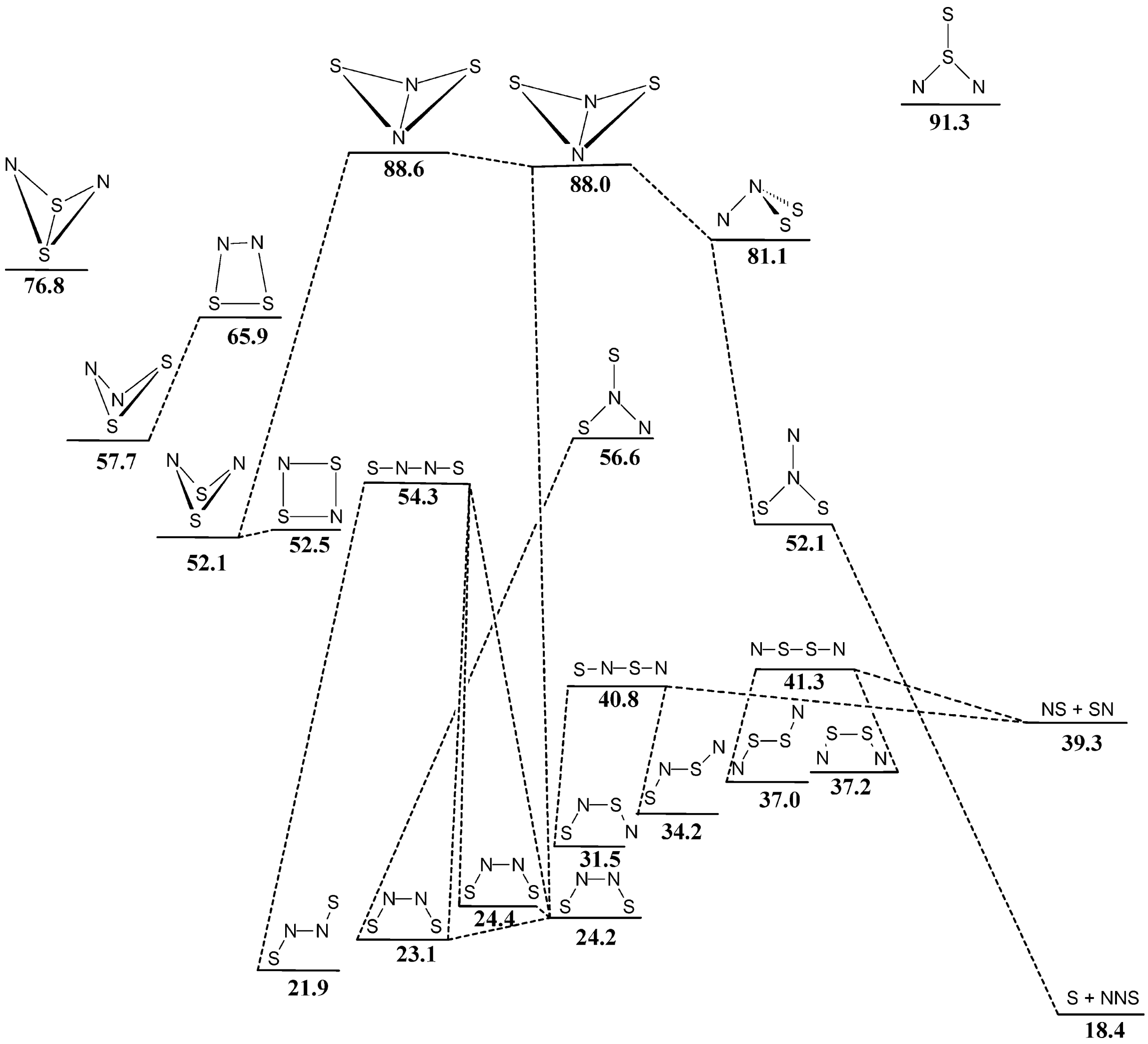


Figure 2. Relative energies (in kcal/mol) of all stationary points on the lowest triplet potential energy surface of S_2N_2.

number of intermediates, including S_3N_3, which recondense to form $(SN)_x$.[8,9] To explain the gas-phase results, a three-dimensional coupling occurs between planes of $(SN)_x$[9] and possibly S_2N_2. The predicted results for the relevant systems are collected in Figure 7b. Data for both singlet and triplet species are included since the mechanism of polymerization is known to involve a surface crossing (i.e., an ESR signal is generated during the reaction[7]).

The most extensive previous examination of the triplet surface concentrated on two isomers, the square planar isomer of S_2N_2, R2, and the *cis*-SNSN chain, C3.[12] In the CI study, the lowest triplet excited electronic state of R2, $^3B_{3u}$, was approximately 70 kcal/mol above the X^1A_g ground state minimum. At the geometry of a single S_2N_2 unit in $(SN)_x$, the lowest triplet electronic state of the C3 isomer, $1^3A''$, had an energy relative to X^1A_g of 55.1 kcal/mol. Adiabatically these two triplet states are predicted herein to lie 40.5 and 19.5 kcal/mol, respectively, above R2. For both states, the geometry relaxation is significant. In triplet R2, the four SN distances each increase by 0.124 Å relative to the singlet R2 species. For the C3 isomer, the bond lengths change by 0.307, 0.052, and 0.127 Å in comparison to the same singlet structure. The adiabatic excitation energies should be appreciably smaller than the vertical values. Vertical and adiabatic energy differences between the two excited triplet states are similar, though.

The complexity of the potential surface at 20 and 30 kcal/mol above the minimum, as shown in Figure 7b, is obvious. The predicted transition state for the one bond cleavage, whereby R2 become C3, has an open-chain gauche structure, G3, and an activation energy of 47.9 kcal/mol. This is consistent with the observed activation energy of 41 kcal/mol.[34,35] However, there are other singlet and triplet species that are lower in energy, including the G3 transition state which connects C3 and T3. The equivalent triplet structures, C3 and T3, as well as the third-order saddle point, L3 (which connects these two isomers and the SN + SN dissociation channel), are also lower in energy. The previously proposed mechanism involves several higher energy species and thus another mechanism is considered.

As shown in Figure 7b, the reported activation energy is also consistent with excitation to the triplet state of the square planar species, R2. On the triplet surface, the square planar system is a transition state which relaxes to a puckered

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(34) Kanazawa, H.; Stejny, J.; Keller, A. *J. Mater. Sci.* **1990**, *25*, 3838.
(35) Kanazawa, H.; Stejny, J.; Keller, A. *J. Mater. Sci.* **1991**, *26*, 1635.

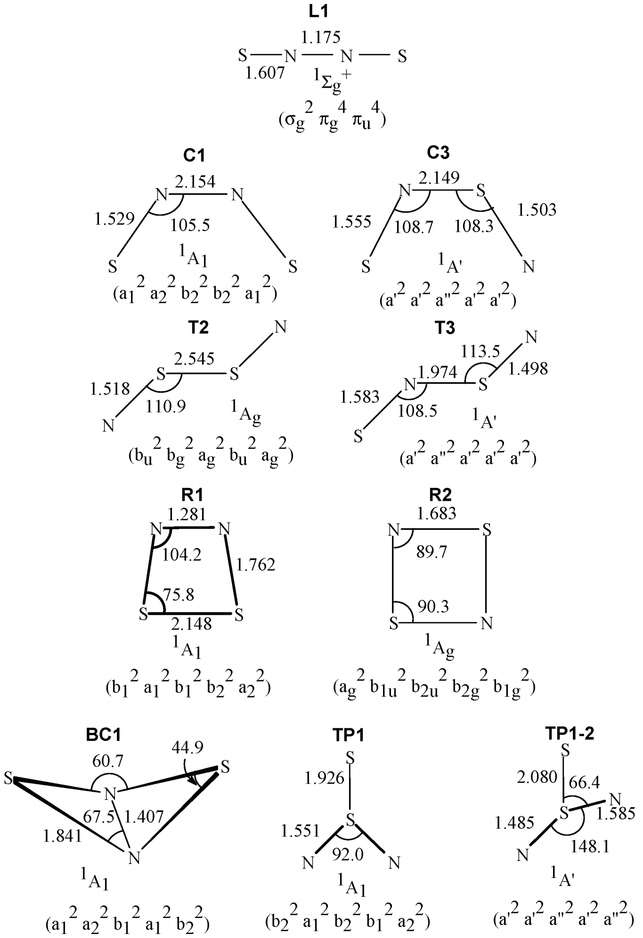

Figure 3. Geometries of the minima on the singlet potential energy surface of S_2N_2. The symmetries of the five HOMOs also are presented.

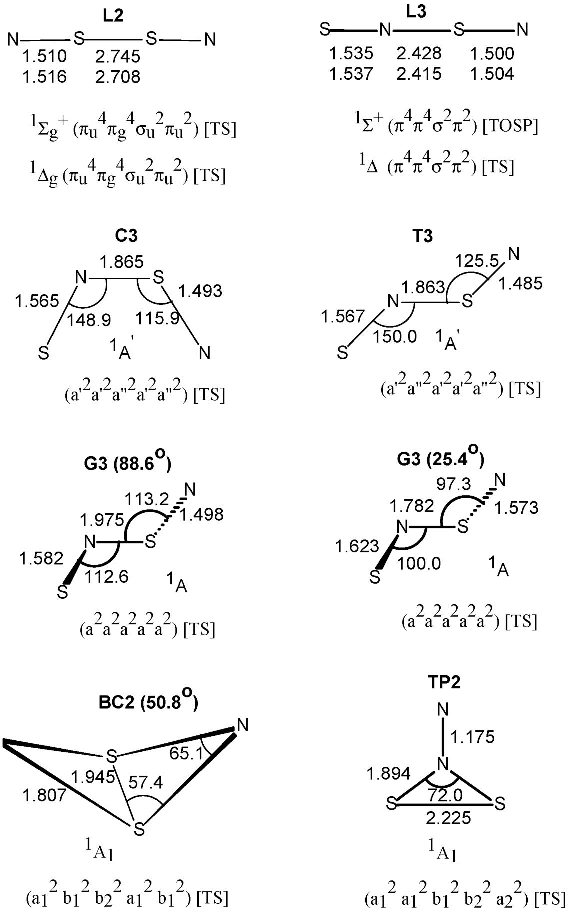

Figure 4. Geometries of the first (TS) and one-third order (TOSP) stationary points on the lowest singlet potential energy surface of S_2N_2. The symmetries of the five HOMOs also are presented.

minimum, R4. This motion lowers the energy only slightly (0.4 kcal/mol), and there is little geometrical change other than the puckering of the ring. The angle of puckering is 19.2°. R4 is not connected with any triplet species other than R2 and will not isomerize or dissociate on the triplet surface and so should be a long-lived species. A mechanism involving R4 is consistent with the observation of an intermediate that produces an ESR signal.

Such a puckering mechanism corresponds to the generally accepted concept of a least-motion approach to the polymerization in the solid state.[6] However, if R4 is to be the intermediate species in the polymerization, then the reaction must occur in a direction approximately perpendicular to the S_2N_2 plane in the crystal, counter to the generally accepted mechanism.[6] This approach, nevertheless, is consistent with the three-dimensional coupling proposed for the formation and subsequent condensation of species in the vapor phase.[9] The basic idea of vertical excitation to a triplet square planar species that puckers on route to $(SN)_x$ should be applicable in the solid state.

3.D. Identity of the Observed Second Isomer of S_2N_2. The more recently observed isomer of S_2N_2 was obtained by seeding a nitrogen/argon discharge with sulfur vapor and condensing the products in an argon matrix.[13] The main nitrogen and sulfur-containing molecules observed in that study were SN, SSN, NSN, and NSS. An IR frequency at 1167.5 cm^{-1} was assigned to a new isomer of S_2N_2. Two previous theoretical treatments have addressed the identity of this new species. Warren et al.[14] limited their discussion to the three lowest energy structures L1, R1, and R2 and concluded that the new species is R1 with a predicted vibrational frequency of 1116 cm^{-1}. Somasundram and Handy,[15] with DFT, found that none of these three structures possessed a vibrational frequency in agreement with experiment. The frequencies of other isomers were not considered, and the identity of the species is still uncertain. The vibrational frequencies of all diatomic, triatomic, and tetraatomic minima predicted in this study are given in Table 3. The results will first be compared with experiment.

Huber and Herzberg[27] reported vibrational frequencies of 2359 and 1461 cm^{-1} for the $X^1\Sigma_g^+$ and excited $a^3\Sigma_u^+$ states of N_2. The present predicted values are larger by 85 and 104 cm^{-1}, respectively. For diatomic sulfur, the experimentally observed frequencies for $X^3\Sigma_g^-$ and $a^1\Delta_g$ are 726 and 702 cm^{-1}. The present prediction is 27 cm^{-1} too small for the $X^3\Sigma_g^-$ ground state. According to Huber and Herzberg,[27] the heteronuclear diatomic molecule SN has a vibrational frequency of 1219 cm^{-1} in the $X^2\Pi$ ground state. A result that is smaller by 21 cm^{-1} is predicted. A more recent gas-phase determination[36] of the vibrational frequency of SN gave

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(36) Matasumura, K.; Kawaguchi, K.; Nagai, K.; Yamada, C.; Hirota, E. *J. Mol. Spectrosc.* **1980**, *84*, 68.

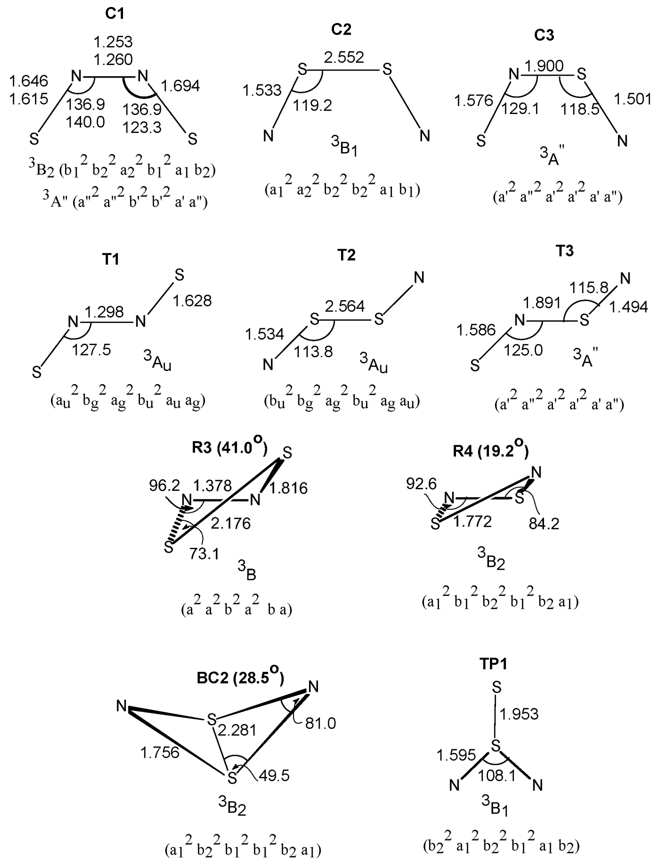

Figure 5. Geometries of the minima on the lowest triplet potential energy surface of S_2N_2. The symmetries of the four highest doubly occupied and two singly occupied molecular orbitals also are shown.

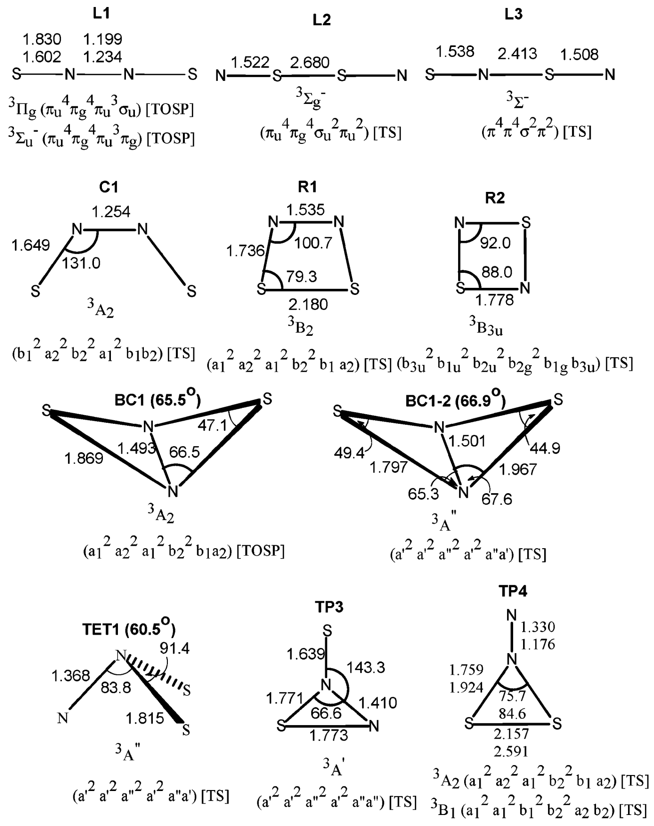

Figure 6. Geometries of the first- (TS) and third-order (TOSP) stationary points on the lowest triplet potential energy surface of S_2N_2. The symmetries of the four highest doubly and two singly occupied molecular orbitals also are presented.

1204 cm^{-1}, decreasing the difference from the present prediction to 6 cm^{-1}. The predicted S_2N_2 values ultimately will be compared with the matrix isolation experimental values of Hassanzadeh and Andrews.[13] The present predictions for some of the smaller molecules may be compared with the results from their matrix isolation studies to assess effects due to the environment.

Five of the systems computed in the present work were assigned to IR absorptions observed in the matrix isolation experiments in argon.[13] The vibrational band corresponding to SN was found at 1209.4 cm^{-1}, the SNS peaks were at 659.7 and 1225 cm^{-1}, the SSN bands were observed at 594.6 and 1017.1 cm^{-1}, and a frequency of 2040.2 cm^{-1} was correlated with the most stable N_2S isomer. Square planar S_2N_2 had bands at 472, 666, and 788 cm^{-1}. Most of the present predicted frequencies are within 40 cm^{-1} of the experimental values.

For the three lowest energy isomers of S_2N_2, higher level theoretical predictions can also be compared with the present values. Warren et al.[14] report frequencies at the MP2 level of theory using two different basis sets, 6-311G(2df) and 6-311++G(3df). Somasundram and Handy[15] published B3LYP/TZ2P vibrational frequencies. The present predictions will be compared with the MP2 and DFT results which used the larger basis sets.

For L1, MP2 predicted values (in cm^{-1}) of π_u 152, π_g 116, σ_g 551, σ_u 1037, and σ_g 1910. B3LYP yielded the corresponding frequencies of 156, 335, 520, 934, and 2196 cm^{-1}. For all vibrations, the present predictions (Table 3) are in closer agreement with the earlier DFT results. The MP2 predictions for the vibrational frequencies of L1 are not far from the present results except for the π_g mode.

The MP2 results for R1 were (in cm^{-1}) b_2 500, a_2 499, a_1 516, a_1 771, b_2 859, and a_1 1116. B3LYP predicted 439, 498, 482, 655, 845, and 1408 cm^{-1} for the respective frequencies. The present results are in good agreement with the B3LYP/TZ2P predictions. The one large variation between the MP2 and the earlier and present B3LYP results is for the highest a_1 frequency. MP2 predicts a value of 1116 cm^{-1} while both DFT predictions are roughly 300 cm^{-1} larger at approximately 1400 cm^{-1}. The conclusion of the earlier DFT study, that R1 is not the isomer observed by Hassanzadeh and Andrews,[13] is supported further by the present theoretical study.

Warren et al.[14] predicted MP2 frequencies (in cm^{-1}) of b_{3u} 475, a_g 620, b_{1u} 783, b_{2u} 791, a_g 851, and b_{3g} 886 for R2. The respective B3LYP results of Somasundram and Handy[15] were 477, 643, 650, 777, 938, and 922 cm^{-1}. The present and earlier B3LYP results agree with each other while the MP2 values differ, especially at higher values. The one disagreement is the order of the highest two vibrations. The b_{3g} mode is predicted to be lower than the a_g mode at the B3LYP/TZ2P level of theory.

To resolve the issue of the structure of the newly observed isomer, all minima on both potential energy surfaces were examined in search of a structure with a vibrational frequency

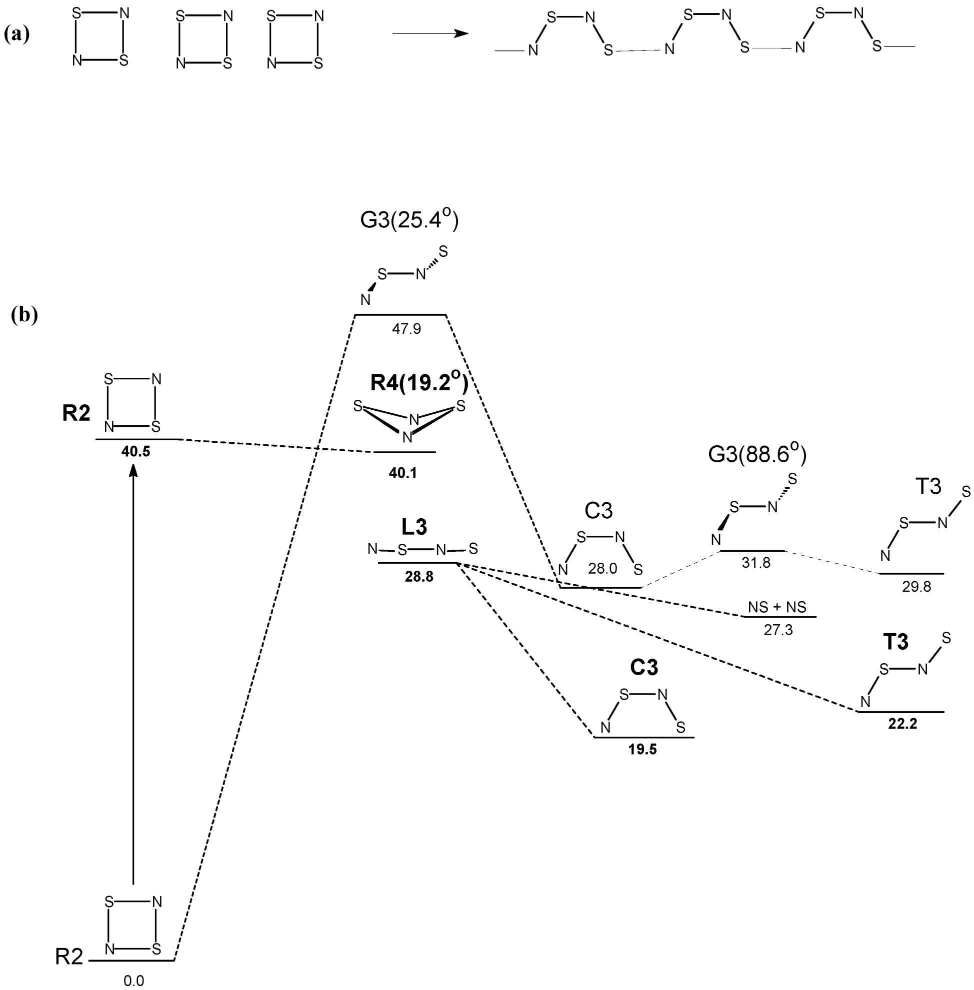

Figure 7. (a) Schematic of the generally accepted mechanism of formation of $(SN)_x$. (b) Important species in the proposed mechanism for the polymerization of S_2N_2 to $(SN)_x$. Relative energies are in kcal/mol. Species on the triplet surface are in bold.

close to that observed experimentally. On the basis of the frequencies and intensities, possibilities were reduced from 21 minima to the 7 minima that are presented in bold in Table 3. Singlet C1 has a b_2 mode at 1172 cm^{-1}, singlet C3 has a mode of a′ symmetry at 1237 cm^{-1}, triplet C3 has an a′ mode at 1171 cm^{-1}, singlet T3 has an a′ mode at 1229 cm^{-1}, triplet T3 has an a′ mode at 1204 cm^{-1}, singlet T2 has a b_u mode at 1143 cm^{-1}, and triplet C2 has an a_1 mode at 1118 cm^{-1}.

The new S_2N_2 isomer was observed in experiments where SN was produced. The observed frequency for the SN radical in argon is 11.4 cm^{-1} greater than that predicted for isolated SN. The anticipated shift for the vibration of the new isomer may be similar. A decrease in the experimental frequency of the new isomer by 11.4 cm^{-1} gives a value of 1156 cm^{-1}. The closest match exists for singlet T2 (in bold and italic in Table 3). This structure agrees with the tentative assignment by Hassanzadeh and Andrews.[13]

In their experiments they observed that, when the reservoir temperature was increased from 50 to 70 °C, the intensity of the new band, relative to that of SN at 1209.4 cm^{-1}, increased from a ratio of 1:2 to 1:1. When the sample was annealed, the new band disappeared.

The present results place the C_{2h} ^1A_g minimum of T2 8.1 kcal/mol above the SN dissociation limit (Figure 1). If the two species are in equilibrium, then this energy difference should correspond to the ratio of reactants (SN + SN) and products (T2) in the Boltzmann distribution (eq 1).

$$2SN \rightleftharpoons \text{T2 isomer of } S_2N_2$$

$$\frac{N(SN + SN)}{N(T2)} = e^{\left(\frac{8.01\ \text{kcal}\cdot\text{mol}^{-1}}{(0.00199\ \text{kcal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \times T(\text{K}))}\right)} \qquad (1)$$

At 50 °C, the ratio of reactants to products is ~258000. When the reaction temperature is increased to 70 °C, the ratio drops to ~125000. This demonstrates that the concentration of the product, T2, with respect to the reactant has doubled, as should the intensity of the observed product band, consistent with experiment.

3.E. Formation of Other Possible Isomers. The isomer identified by Hassanzedah and Andrews[13] probably corresponds to the *trans*-NSSN species, T2, on the singlet surface. Is this species the only isomer capable of being formed by the dimerization of two SN units? The formation and dissociation pathways of various S_2N_2 isomers have been predicted. Warren et al. considered such processes but focused on only the three lowest isomers, L1, R1, and R2.[14] The formation of L1 was considered to be symmetry forbidden, but the formations of the two ring systems, R1

Table 3. Predicted Harmonic Vibrational Frequencies and IR Intensities[a]

molecule	electronic state	vibration(s)					
				diatomics			
SN	$^{2}\Pi$	(σ) 1198 (16)					
	$^{4}\Sigma^{-}$	(σ) 898 (0)					
S_2	$^{3}\Sigma_{g}^{-}$	(σ_{g}) 699 (0)					
	$^{1}\Sigma_{g}^{+}$	(σ_{g}) 695 (0)					
N_2	$^{1}\Sigma_{g}^{+}$	(σ_{g}) 2444 (0)					
	$^{3}\Sigma_{u}^{-}$	(σ_{g}) 1565 (0)					
				triatomics			
SNS	$^{2}A_{1}$	(a_1) 281 (3)	(a_1) 668 (2)	(b_2) 1214 (377)			
SSN	$^{2}A'$	(a') 220 (14)	(a') 569 (17)	(a') 842 (38)			
NNS	$^{1}\Sigma^{+}$	(π) 453 (0)	(σ) 759 (28)	(σ) 2178 (329)			
NSN	$^{1}A_{1}$	(b_2) 426 (3)	(a_1) 483 (8)	(a_1) 1896 (73)			
	$^{1}\Sigma_{g}^{+}$	(π_u) 246 (5)	(σ_g) 1025 (0)	(σ_u) 1392 (18)			
				S_2N_2			
L1	$^{1}\Sigma_{g}^{+}$	(π_u) 156 (0)	(π_g) 243 (0)	(σ_g) 513 (0)	(σ_u) 916 (286)	(σ_g) 2223 (0)	
R1	$^{1}A_{1}$	(b_2) 436 (11)	(a_2) 469 (0)	(a_1) 494 (4)	(a_1) 671 (25)	(b_2) 831 (281)	(a_1) 1436 (70)
R2	$^{1}A_{g}$	(b_{3u}) 447 (23)	(a_g) 631 (0)	(b_{1u}) 656 (4)	(b_{2u}) 749 (31)	(a_g) 907 (0)	(b_{3g}) 921 (0)
T1	$^{3}A_{u}$	(b_u) 119 (46)	(a_u) 170 (1)	(a_g) 399 (0)	(a_g) 846 (0)	(b_u) 880 (90)	(a_g) 1215 (0)
C1	$^{1}A_{1}$	(a_1) 117 (7)	(a_2) 151 (0)	(a_1) 258 (2)	(b_2) 439 (1)	(b_2) **1172** (268)	(a_1) 1188 (12)
	$^{3}B_{2}$	(a_1) 155 (1)	(a_2) 314 (0)	(b_2) 345 (21)	(a_1) 638 (6)	(b_2) 759 (56)	(a_1) 1597 (50)
	$^{3}A''$	(a') 133 (2)	(a') 366 (99)	(a'') 456 (0)	(a') 609 (3)	(a') 776 (22)	(a') 1449 (286)
C3	$^{1}A'$	(a') 120 (1)	(a'') 137 (18)	(a') 241 (0)	(a') 447 (4)	(a') 1099 (119)	(a') **1237** (82)
	$^{3}A''$	(a') 148 (1)	(a'') 193 (18)	(a') 320 (39)	(a') 378 (32)	(a') 1029 (58)	(a') **1171** (89)
T3	$^{1}A'$	(a'') 43 (2)	(a') 171 (3)	(a') 237 (4)	(a') 519 (28)	(a') 1042 (22)	(a') **1229** (55)
	$^{3}A''$	(a') 103 (0)	(a') 172 (1)	(a') 259 (14)	(a') 640 (6)	(a') 1009 (48)	(a') **1204** (107)
T2	$^{1}A_{g}$	(a_u) 69 (18)	(b_u) 71 (14)	(a_g) 176 (0)	(a_g) 381 (0)	(b_u) ***1143*** (307)	(a_g) 1210 (0)
	$^{3}A_{u}$	(a_u) 108 (12)	(b_u) 120 (7)	(a_g) 168 (0)	(a_g) 290 (0)	(b_u) 938 (749)	(a_g) 1114 (0)
C2	$^{3}B_{1}$	(a_1) 93 (3)	(a_2) 140 (0)	(a_1) 221 (1)	(b_2) 248 (1)	(b_2) 944 (617)	(a_1) **1118** (25)
BC1	$^{1}A_{1}$	(a_1) 323 (4)	(a_2) 395 (0)	(a_1) 524 (3)	(b_1) 590 (5)	(b_2) 634 (28)	(a_1) 1055 (10)
BC2	$^{3}B_{2}$	(a_1) 356 (13)	(a_1) 527 (5)	(b_1) 648 (15)	(b_2) 654 (40)	(a_1) 765 (0)	(a_2) 1263 (0)
TP1−2	$^{1}A_{1}$	(b_1) 447 (23)	(a_1) 631 (0)	(a_1) 657 (4)	(b_2) 750 (31)	(a_1) 908 (0)	(b_2) 922 (0)
	$^{1}A'$	(a'') 240 (8)	(a'') 247 (2)	(a') 447 (51)	(a') 518 (6)	(a') 906 (4)	(a') 1345 (44)
	$^{3}B_{1}$	(b_2) 114 (6)	(b_1) 232 (1)	(a_1) 290 (13)	(a_1) 565 (13)	(b_2) 601 (6)	(a_1) 929 (13)
R3	^{3}B	(b) 70 (8)	(a) 286 (27)	(a) 429 (1)	(a) 475 (3)	(b) 613 (5)	(a) 898 (3)
R4	$^{3}B_{2}$	(a_1) 203 (13)	(a_1) 492 (0)	(b_2) 559 (6)	(a_2) 616 (0)	(b_1) 659 (1)	(a_1) 731 (2)

[a] Frequencies in cm^{-1}, intensities in km/mol.

and R2, were not. Both were viewed as plausible products of the dimerization of SN. Recall their prediction that R1 was the observed isomer. However, since Hassanzadeh and Andrews did not observe the square planar species, R2, during the process,[13] Warren et al.[14] could not unambiguously explain the experimental results. Although the reaction may be allowed, the breaking of the strong bonds in the ring systems inevitably must overcome a considerable barrier. Thus, the focus herein is on linear and bent structures of S_2N_2 and their possible formation from SN radicals.

The only linear molecule which is a minimum is the closed shell singlet SNNS, L1. Its electronic configuration $(...\sigma_g^2\,\pi_g^4\,\pi_u^4)$ is very stable. Moreover this configuration does not correlate with that of two ground-state SN radicals, each with $(...\sigma^2\,\pi^2\,\pi^1)$, and L1 cannot be directly formed from two SN radicals, as was concluded previously.[14] On the triplet surface, both L1 states are saddle points and correspond to an excitation of the π_u electron into either the σ_u or π_g orbitals (Figure 6). Neither of these states of triplet L1 directly correlates with two SN units. However, the vibrational characterizations of these two linear triplets indicate that both saddle points display Renner−Teller splittings[37] in the π vibrational modes. To examine these splittings and their effect on the observation of cis and trans isomers, symmetric cuts (5° increments) through the bending potential energy surfaces (i.e., restricted to C_{2v} and C_{2h} symmetry) were followed for each possible state arising from three electronic configurations of L1: $^{1}\Sigma_g^{+}$ $(...\sigma_g^2\,\pi_g^4\,\pi_u^4)$, $^{3}\Sigma_u^{-}$ $(...\sigma_g^2\,\pi_g^4\,\pi_u^3\,\pi_g^1)$, and $^{3}\Pi_g$ $(...\sigma_g^2\,\pi_g^4\,\pi_u^3\,\sigma_u^1)$. These are shown in Figures 8 and 9. The bond distances were fixed at those of the linear species. By analyzing the C_{2v} and C_{2h} bending curves for L1, we were able to explain why three triplet C1 isomers, two minima and a transition state which connects them, were found while only one triplet T1 and one singlet C1 isomer exist.

The near absence of T1 isomers is related to the lack of features in the C_{2h} bending curves. Only one of the curves, $^{3}A_u$, leads to a minimum (Figure 8). The C_{2v} bending curves on the other hand are more complex, as shown in Figure 9. Note that the $^{1}A_1$ curve is repulsive up to a bending angle of about 120° where it starts to become attractive, consistent with the observation of a singlet C1 isomer with an angle of 105.5° (Figure 3). The barrier to formation of this isomer corresponds to the energy maximum on the bending curve, or ca. 35 kcal/mol. No other C_{2v} (or C_{2h}) electronic state arises from the closed shell singlet configuration of L1 and therefore it is the only singlet isomer observed. On the triplet surface, the lower $^{3}A_2$ and $^{3}B_2$ curves cross at an angle of ca. 131°. This region corresponds to that of the $^{3}A_2$ transition state, C1. Its IRC leads to the $^{3}B_2$ minimum, which has a

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(37) Lee, T. J.; Fox, D. J.; Schaefer, H. F., III; Pitzer, R. M. *J. Chem. Phys.* **1983**, *81*, 356.

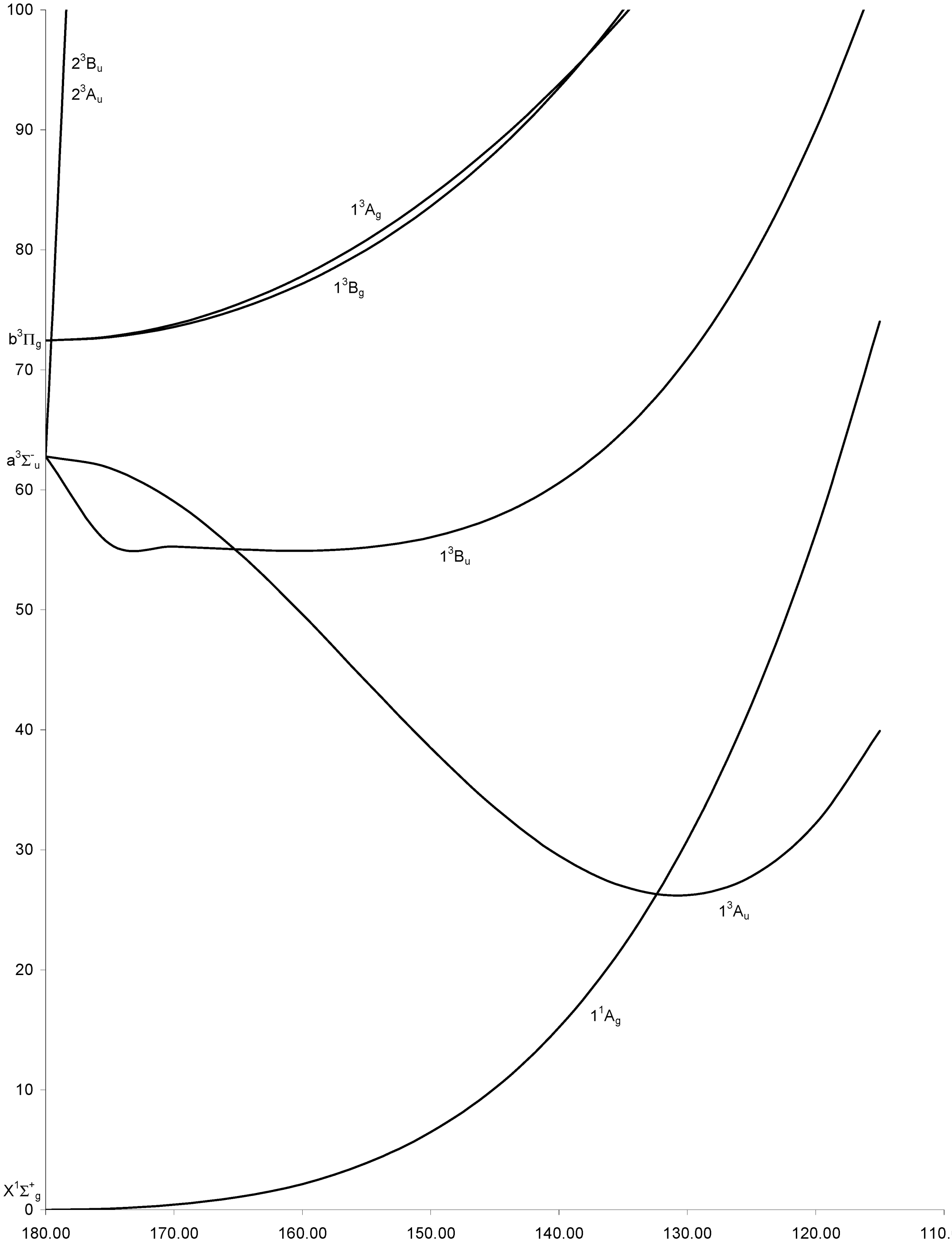

Figure 8. C_{2h} (trans) bending curves of L1 and their relationships to the formation of the ^3A_u T1 isomer.

bond angle of approximately 137°, corresponding to the minimum in the $^3B_2$ curve, and the $^3A''$ minimum, which has a structure with bond angles of 140 and 123° (Figure 5), which are a combination of the two C_{2v} bending minima angles. These findings are similar to those for the NO dimer.[38]

The two other linear systems, L2 and L3, have $\pi_g^4\ \sigma_u^2\ \pi_u^2$ electronic configurations and can correlate with two ground-state SN radicals, each with a $(...\sigma^2\ \pi^2\ \pi^1)$ electronic configuration. If two SN units dimerize to form *trans*-NSSN, why would they not also give *cis*-NSSN or *cis*- and *trans*-SNSN? The bending curves again can provide insight. They are, however, very complex, and for L3 the problem is three-dimensional (i.e., there are two separate bending degrees of freedom) and so will not be presented in full. However, a brief summary of the general results is given pictorially in Figure 10.

Three electronic states arise from the $\pi_g^4\ \sigma_u^2\ \pi_u^2$ electronic configuration, $^3\Sigma^-$, $^1\Delta$, and $^1\Sigma^+$. As seen in Figure 10, the lowest state is $^3\Sigma^-$, as expected from Hunds rules. It is

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(38) Sayós, R.; Valero, R.; Anglada, J. M.; González, M. *J. Chem. Phys.* **2000**, *112*, 6608.

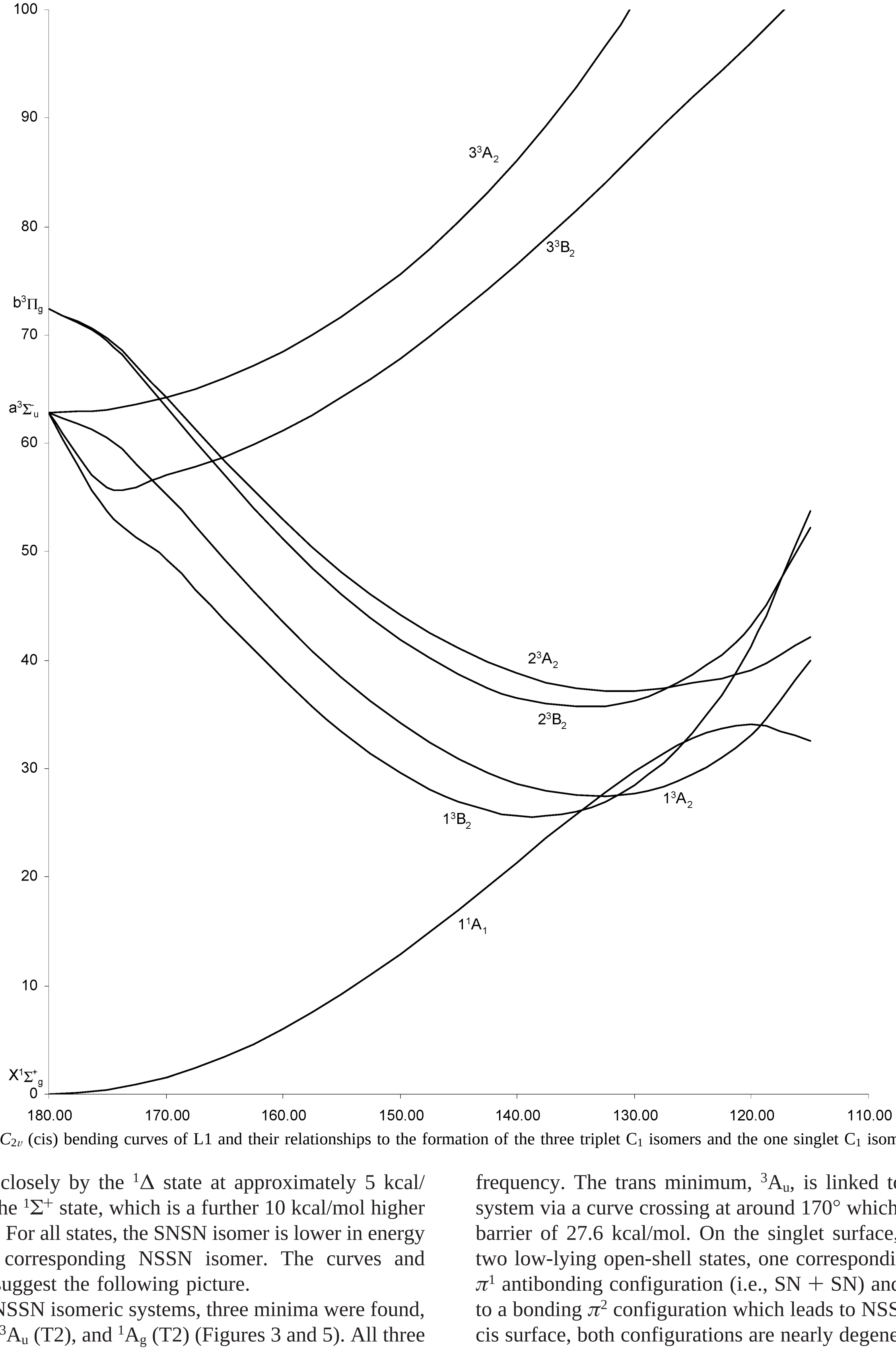

Figure 9. C_{2v} (cis) bending curves of L1 and their relationships to the formation of the three triplet C_1 isomers and the one singlet C_1 isomer.

followed closely by the $^1\Delta$ state at approximately 5 kcal/mol and the $^1\Sigma^+$ state, which is a further 10 kcal/mol higher in energy. For all states, the SNSN isomer is lower in energy than the corresponding NSSN isomer. The curves and surfaces suggest the following picture.

In the NSSN isomeric systems, three minima were found, $^3B_1$ (C2), ^3A_u (T2), and ^1A_g (T2) (Figures 3 and 5). All three correlate, through the bending curves, to the linear systems and could be formed by the dimerization of SN. Both $^3B_1$ (C2) and ^3A_u (T2) originate from the $^3\Sigma_g^-$ bending curves. The cis minimum, $^3B_1$, lies 4.1 kcal/mol lower in energy and is the corresponding minimum of the $^3\Sigma_g^-$ imaginary frequency. The trans minimum, ^3A_u, is linked to the $^3\Sigma_g^-$ system via a curve crossing at around 170° which induces a barrier of 27.6 kcal/mol. On the singlet surface, there are two low-lying open-shell states, one corresponding to a $\pi^1\pi^1$ antibonding configuration (i.e., SN + SN) and the other to a bonding π^2 configuration which leads to NSSN. On the cis surface, both configurations are nearly degenerate along the bending coordinate and collapse upon each other at a bending angle of ca. 120° and therefore correlate with SN + SN dissociation. This explains why previous[14,15] and present theories do not find a singlet *cis*-NSSN when correlated methods are used. On the trans surface, the two

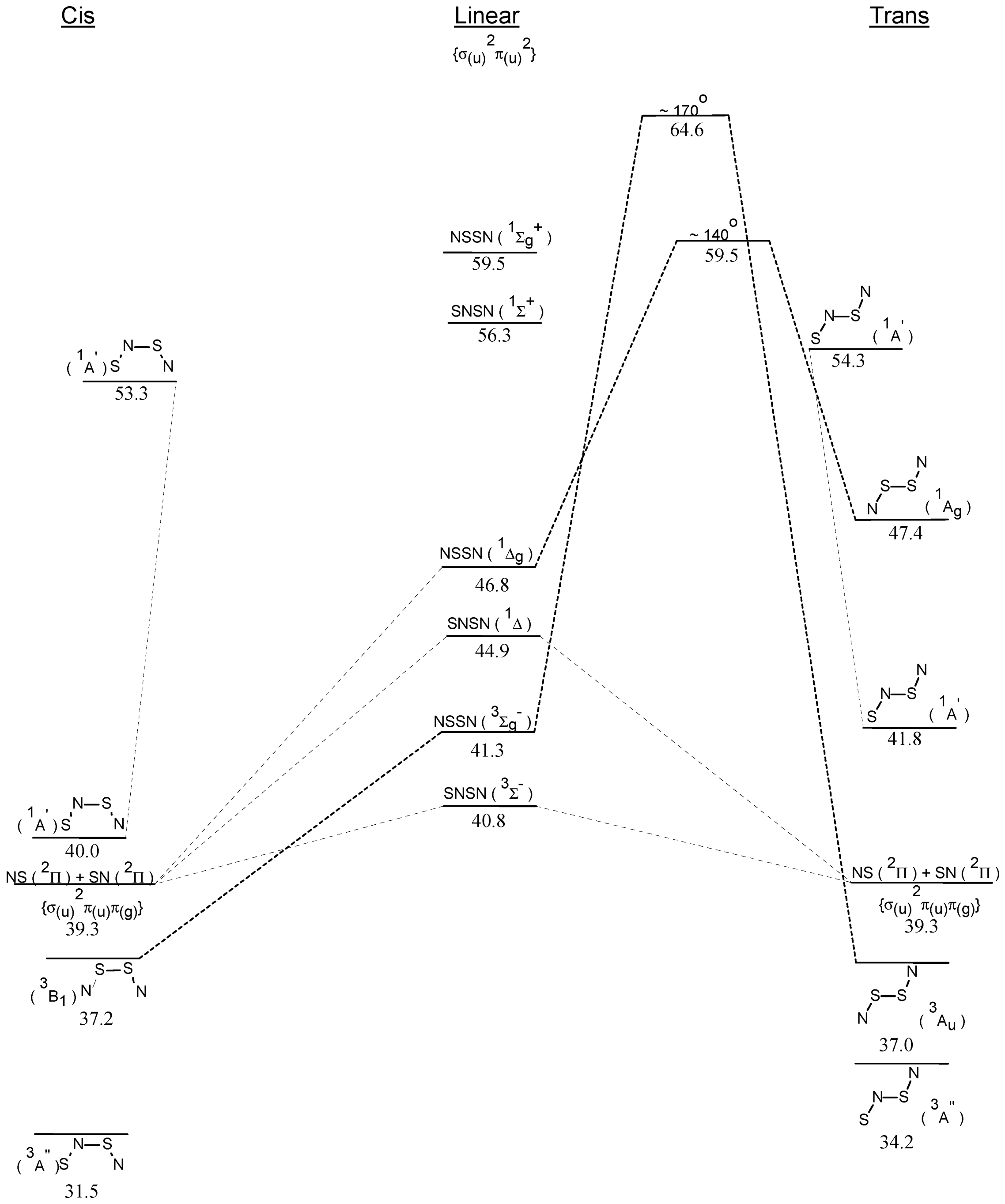

Figure 10. Relative energies (in kcal/mol) of selected stationary points on the singlet and triplet potential energy surfaces of S_2N_2 and their correlation with the linear species.

open-shell configurations separate as one proceeds along the bending curve and at an angle of ca. 140° the higher lying open shell and the closed shell curves cross, imposing a barrier of ca. 13 kcal/mol.

For the bent SNSN isomeric systems, four minima and two saddle points were found (see Figures 3−5). On the singlet surface, the higher lying C3 and T3 transition states connect with the corresponding minima. As in the singlet NSSN case, two low-lying open-shell states, one corresponding to a $\pi^1\pi^1$ antibonding configuration and the other to a bonding π^2 configuration, exist. In this case, all low energy bending surfaces, both singlet and triplet, prefer the $\pi^1\pi^1$ antibonding electronic configuration and correlate directly with the SN + SN dissociation limit. Hence, all bent SNSN isomers correlate with higher excited states. This prohibits the formation of SNSN isomers from the dimerization of SN.

These results show that it may be possible to form other NSSN isomers. Returning to the original question: why is T2 (^1A_g) the only experimentally observed isomer? Two issues must be considered. First is the barrier to formation/dissociation. In the case of C2 ($^3B_1$), the linear species lies only 4 kcal/mol higher in energy. This makes this minimum very weakly bound energetically and so will be fairly short-lived. On the trans surface, the T2 (^3A_u) barrier is ca. 27 kcal/mol whereas the T2 (^1A_g) barrier is roughly half this value. Both are considered long-lived species. However, the rate of formation, which also is dependent on these barriers, favors the formation of the singlet species. Second, the reactivity of a triplet species, especially in the presence of other radicals such as SN, must be considered. Thus, even if C2 ($^3B_1$) and/or T2 (^3A_u) were formed in an argon matrix, they would react readily with their equilibrium partner, the SN radical, to form other species, such as NSS and NSN, both of which were observed in the experiment. Combining these two issues, it is easily understood why the only S_2N_2 species observed is T2 (^1A_g).

4. Conclusions

A fairly extensive mapping of the singlet and triplet potential energy surfaces of S_2N_2 has been presented. The minima that were predicted in previous studies also were obtained here. For the *cis*-NSSN and *cis*-SNSN chains, an explanation has been proffered of why they were not observed with methods such as B3LYP or MP2. For the *cis*-NSSN isomer, an open-shell configuration leads to dissociation into SN + SN, and for the *cis*-SNSN isomer, two closed-shell electronic configurations were possible, one corresponds to a minimum and the other to a transition state. The potential energy surface is very complex.

Several possible mechanisms of the S_2N_2 polymerization have been considered. The commonly accepted mechanism proceeds through a region where the electronic nature of the surface is very complex. This makes this mechanism unlikely. A second possible mechanism was considered that is consistent with experiment. It is proposed that $(SN)_x$ is formed after an intersystem crossing following a vertical excitation of square planar S_2N_2. The triplet species then relaxes by a puckering motion and polymerization occurs in a direction approximately perpendicular to the mean plane of the ring.

The identity was predicted of the other isomer of S_2N_2 that has been observed. On the basis of vibrational frequencies and intensities, energy differences, and pathways for dimerization of SN, the structure observed in the sulfur/nitrogen/argon discharge is predicted to be *trans*-NSSN. This is the only product formed upon dimerization of the SN radical.

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