products were removed and purification was accomplished by fractional condensation and gas chromatography.

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Registry No. $(CF_3)_2S{=}NH$, 60646-40-4; $(CF_3)_2S{=}NCH_3$, 60646-41-5; $(CF_3)_2S{=}NCH_2CH_3$, 60646-42-6; $(CF_3)_2S{=}NCH(CH_3)_2$, 60646-43-7; $(CF_3)_2S(O){=}NCH_2CH_3$, 60646-44-8; $(CF_3)_2S(O){=}NCH(CH_3)_2$, 60646-45-9; $(CF_3)_2SF_2$, 30341-38-9; CH_3NH_2, 74-89-5; $CH_3CH_2NH_2$, 75-04-7; $(CH_3)_2CHNH_2$, 75-31-0; NH_3, 7664-41-7.

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Contribution from the Department of Chemistry,
University of Georgia, Athens, Georgia 30602

Conformational Analysis. 121. Elemental Sulfur

JAMES KAO and NORMAN L. ALLINGER*

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A force field has been developed to permit molecular mechanics calculations on various molecular structures of elemental sulfur. The conformational characteristics of sulfur rings containing 5–12, 14, 16, 18, or 20 sulfur atoms have been examined. Comparison with experimental data is made in all cases where such data exist, and predictions are made for other cases. Ab initio molecular orbital calculations using an STO-3G basis set were carried out for *cyclo*-hexasulfur and are consistent with the molecular mechanics calculations in indicating that the chair and the twist forms are two stable conformations, with the chair about 15 kcal/mol more stable, while the boat (C_{2v}) is a twist–twist rotational transition state.

Elemental sulfur[3,4] can exist in a polymeric form and as a variety of rings containing different numbers of sulfur atoms, many of which have been isolated. The molecular structures of only a few of these different allotropes have so far been studied. The most straightforward way of determining the structures and conformations of these sulfur allotropes would be by electron diffraction and x-ray diffraction. The ring structures of S_6, S_8, S_{12}, S_{18}, and S_{20}, have been studied[5–9] by the x-ray method, but the accuracy for most compounds is generally not too high. Only a preliminary structure of S_7 has been reported. The structures of S_9, S_{10}, and S_{11} have not yet been studied experimentally. The x-ray method is the only experimental technique so far having been used. No sulfur allotrope appears to have yet had its structure studied experimentally in the gas phase.

On the other hand, a variety of theoretical methods are also readily applicable to the conformational study of these compounds. The molecular mechanics or force field method[10] has been successful in calculating the structures and energies of a variety of types of related compounds including thiaalkanes,[11] sulfoxides,[12] disulfides,[13,14] and polysulfides.[13] In the present work, the molecular mechanics method has been applied to the conformational study of elemental sulfur.

The Molecular Mechanics Method

The method previously developed for the calculation of the structures and energies of disulfides[13] was used as a starting point, and these force field calculations were extended to a study of elemental sulfur. *cyclo*-Hexasulfur was the only sulfur allotrope examined in our preliminary study.[13] In the present study, *cyclo*-hexasulfur,[5] *cyclo*-octasulfur (α_{15}),[6] *cyclo*-dodecasulfur,[7] *cyclo*-octadecasulfur (α),[8] *cyclo*-icosasulfur,[8b,9] and fibrous sulfur[15] were used as model compounds from which to obtain the necessary force field parameters. Three parameters, the natural bond length of the S–S bond, the natural bond angle for the S–S–S angle, and the S–S–S–S torsional function, were modified from the earlier more approximate values to meet the more demanding experimental observations on compounds included in this study. The S–S–S natural bond angle and the S–S natural bond length are now assigned values of respectively 106.5° and 2.050 Å, while previously 104.0° and 2.024 Å were used.

Our previous assignment for the natural bond length of the S–S bond was based on both the experimental electron diffraction data[16a] and microwave data[16b] for dimethyl disulfide. However, experimental S–S single bond lengths span quite a range (for example, 1.90 Å in FSSF,[17a] 2.03 Å in CH_3SSCH_3,[16] 2.07 Å in $Cl_3CSSCCl_3$,[17b] and 2.10 Å in 1,2-dithiolane-4-carboxylic acid[17c]) and are very sensitive to substituents. The bond length given is clearly better for elemental sulfur. The wide range of S–S single bond lengths is presumably due to secondary environmental effects caused by the lone-pair electrons on the sulfur atoms[18] although experimental error may be a problem in some cases. Dependence of the S–S bond length and the stretching vibration on the dihedral angle was postulated[19] in 1973 and was also made probable by the CNDO/2 calculations[20] for the case of CH_3SSCH_3. But this has been disputed[21] since clearly other effects, e.g., the conformation of the substituents,[22] can also play a part. This problem seems complex and cannot be regarded as convincingly solved. The CNDO/2 results with the spd parameterization in particular gives very questionable results.[14]

Due to the limited scope in this study (to elemental sulfur only) the substituent effect on the S–S bond length will not be further considered here, except that to say we assumed a longer natural bond length relative to the one used for disulfides. It should also be emphasized here that the choice of natural bond length is not critical in our current confor-

Table I. Comparison of Calculated and Observed Geometries[a]

Geometries	Calcd	Obsd
cyclo-Hexasulfur (1961)[5]		
S-S, Å	2.057	2.057 ± 0.018
S-S-S, deg	102.9	102.2 ± 1.6
S-S-S-S, deg	73.3	74.5 ± 2.5
cyclo-Octasulfur (1965)[6]		
S-S, Å	2.047	2.048 ± 0.002
S-S-S, deg	108.1	107.9 ± 0.1
S-S-S-S, deg	98.6	98.6 ± 0.5
cyclo-Dodecasulfur (1966)[7]		
S-S, Å	2.050	2.055 ± 0.010
S-S-S, deg	106.1	106.5 ± 0.5
S-S-S-S, deg	87.8	89.3
cyclo-Octadecasulfur (1974)[8]		
S-S, Å	2.050	2.059 ± 0.003
S-S-S, deg	106.3	106.3 ± 0.1
S-S-S-S, deg	89.5	84.4 ± 0.2
cyclo-Icosasulfur (1974)[9]		
S-S, Å	2.049	2.047 ± 0.005
S-S-S, deg	106.5	106.5 ± 0.2
S-S-S-S, deg	89.3	83.0 ± 0.4
Fibrous Sulfur (1969)[14]		
S-S, Å	2.049	2.07
S-S-S, deg	106.2	106
S-S-S-S, deg	89.0	95

[a] Average values are compared.

mational study since almost identical results can be obtained no matter whether 2.024 or 2.050 Å is used (of course, except the calculated bond lengths). This is due to the fact that torsional strain is the predominant factor in determining the conformations and energies of sulfur allotropes.

The torsional function employed here has a twofold barrier: $V_2(1 + \cos \omega)/2$ where V_2 is 7.6 kcal/mol. (With disulfides, it was found that another component of the barrier, $V_3 = 1.7$ kcal/mol, was required for best results for torsion about the C–S–S–C linkage.) In the absence of information at the time regarding the S–S–S–S linkage, the same value was also used for the latter. Such a term would give poor heats of formation here, and so it was deleted. (This deletion would have a negligible effect on the previous disulfide work.) The use of a twofold rotational barrier is consistent with quantum chemical calculations carried out by various methods.[14] Several explanations[23–25] for this are available: (a) the barrier results from the repulsion between the lone-pair electrons in 3pπ AO's on each sulfur of the central S–S bond and the repulsion is minimized when these AO's are orthogonal; (b) the character of the S–S bond is enhanced when, for example, in HSSH, the S–H bonds are aligned for maximum transfer of electron density through the 3pπ AO's to the hydrogens as in $\mathrm{H—S^+{=}S\ H^-}$; (c) the Mulliken overlap population between the central sulfurs peaks at 90° as the dihedral angle is varied from 0 to 180°.

The natural angle θ for S–S–S depends to some extent on the S–S–S–S torsional barrier. Hence with the changes made in torsion, a change in bending has to be made to compensate. The values used earlier were only approximate, as disulfides were the subject of the work, and tri- and tetrasulfides were examined in only a cursory manner. The adjusted parameter set used here fits the previous data equally well but fits in addition much additional information as given herein. Note that only three parameters were fit in this study.

The experimental and calculated results for all of the compounds used to derive parameters are summarized in Table I. The agreement is generally good. However, one should note that the calculated structure of an isolated molecule is being compared with a crystal structure, and the crystal packing forces may modify significantly the dihedral angles.[10a]

Table II. Steric Energies, Enthalpies, and Bond Energies (kcal/mol)

Molecule	Steric energy[a]	Steric energy[a] per atom	$\Delta H_f°$(g) (calcd)	Bond energy
S_4	49.75	12.45	63.56	49.76
S_5	26.91	5.38	43.51	56.95
S_6	5.35	0.89	24.79	61.52
S_7	9.10	1.30	31.38	61.17
S_8	−0.85	−0.11	24.27	62.62
S_9	4.60	0.51	32.56	62.03
S_{10}	12.00	1.20	42.80	61.37
S_{11}	6.36	0.58	40.00	62.01
S_{12}	−4.75	−0.40	31.73	63.01
S_{14}	10.00	0.71	52.16	61.92
S_{16}	14.63	0.91	62.47	61.75
S_{18}	−8.22	−0.46	45.30	63.12
S_{20}	−8.33	−0.42	51.07	63.10

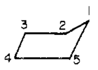
[a] The "steric energy" is the energy given by the program which includes torsion, bending, etc., each relative to its own zero point. When divided by the number of atoms, this gives the strain energy per atom, relative to an arbitrary zero point. Note that several of the structures contain less strain (less enthalpy per atom) than does S_8.

Note that the molecular mechanics program minimizes the energy of the conformation it starts with. It does not find other energy minima. Hence it is necessary for the chemist to select at the outset the conformations to be studied. This was done with the aid of models. Although great care was taken to ensure that all reasonably stable conformations were examined, it is possible that some were missed, especially with the larger rings.

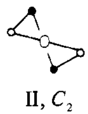
Results and Discussion

cyclo-**Tetrasulfur.** Having now the necessary force field, we first looked at this compound. The S_4 molecule is known to exist in the gas phase, buts its structure is highly speculative; it may be a ring, a diradical, a bipolar compound, or a chain with double bonds.[4,26b] Recent extended Hückel calculations[26b] gave a special stability to a branched structure, sulfur trithiotrioxide. Our force field in the present form is unable to calculate energies for all such possible structures except *cyclo*-tetrasulfur. However, our force field does conclude that *cyclo*-tetrasulfur, if it exists, would indeed be very unstable. It is highly strained with a steric energy almost 10 times of that found in *cyclo*-hexasulfur and an S–S bond energy about 12 kcal/mol smaller than the corresponding value for *cyclo*-hexasulfur (Table II). If S_4 exists in a ring form, the planar form would be the most stable according to our calculations, and the bond length would be 2.083 Å.

cyclo-**Pentasulfur.** As with S_4, we know nothing about this compound (S_5) experimentally beyond the fact that it has been shown to exist in the gas phase.[4] The envelope conformation (I) is calculated to have the same energy as the half-chair (II).



I, C_s


II, C_2

Therefore, the S_5 molecule, like cyclopentane, pseudorotates through a continuum of half-chair forms and envelope forms. The planar form is much less stable than the ground-state conformation (by 11.3 kcal/mol) essentially due to bending and torsion. Since the structure of S_5 is not yet known, our calculated results for both the half-chair and envelope forms are given in Table III.

cyclo-**Hexasulfur.** The geometry is known and a comparison between the experimental and calculated structures is made in Table I. Our calculations predicted that the chair con-

Table III. Calculated Structures

	cyclo-Pentasulfur			*cyclo*-Pentasulfur	
	I	II		I	II
		Distances, Å			
1–2	2.057	2.067	3–4	2.066	2.052
2–3	2.063	2.059			
		Angles, Deg			
1–2–3	99.3	101.9	1–2–3–4	35.6	48.9
2–3–4	103.8	96.8	2–3–4–5	0.0	60.2
5–1–2	95.7	104.4	5–1–2–3	57.3	18.7

	cyclo-Heptasulfur			*cyclo*-Heptasulfur	
	III	IV		III	IV
		Distances, Å			
1–2	2.049	2.048	3–4	2.049	2.054
2–3	2.052	2.049	4–5	2.047	2.043
		Angles, Deg			
7–1–2	106.4	110.7	7–1–2–3	76.4	43.8
1–2–3	104.3	109.7	1–2–3–4	102.4	101.8
2–3–4	106.1	102.8	2–3–4–5	79.6	88.1
3–4–5	111.3	106.6	3–4–5–6	0.0	71.8

	cyclo-Nonasulfur		
	V	VI	VII
	Distances, Å		
1–2	2.049	2.045	2.049
1–9	2.047		
2–3	2.049	2.045	2.043
3–4	2.047	2.047	
4–5	2.054	2.046	
5–6	2.048	2.052	
6–7	2.055		
7–8	2.048		
8–9	2.054		
	Angles, Deg		
2–1–9	107.4	109.7	110.8
1–2–3	103.1	107.4	107.1
2–3–4	107.4	105.4	
3–4–5	107.2	110.8	
4–5–6	107.5	107.3	
5–6–7	108.1		
6–7–8	108.2		
7–8–9	107.6		
1–9–8	107.2		
1–2–3–4	73.7	127.5	136.8
1–9–8–7	67.1		
2–1–9–8	75.3		
2–3–4–5	75.4	83.3	58.7
3–2–1–9	73.7	68.5	
3–4–5–6	67.1	95.6	
4–5–6–7	112.1	128.6	
5–6–7–8	76.5		
6–7–8–9	112.1		

	cyclo-Undecasulfur XI		*cyclo*-Undecasulfur XI
	Distances, Å		
1–2	2.046	6–7	2.049
1–11	2.050	7–8	2.047
2–3	2.047	8–9	2.045
3–4	2.049	9–10	2.050
4–5	2.053	10–11	2.050
5–6	2.053		
	Angles, Deg		
2–1–11	108.6	1–2–3–4	93.4
1–2–3	109.3	1–11–10–9	149.9
2–3–4	105.0	2–1–11–10	61.7
3–4–5	105.9	2–3–4–5	76.5
4–5–6	104.6	3–2–1–11	86.0
5–6–7	105.8	3–4–5–6	85.1
6–7–8	105.0	4–5–6–7	84.9
7–8–9	109.1	5–6–7–8	76.9
8–9–10	108.5	6–7–8–9	93.2
9–10–11	106.5	7–8–9–10	85.9
1–11–10	106.6	8–9–10–11	61.7

	cyclo-Tetradecasulfur			*cyclo*-Tetradecasulfur	
	XVI	XVII		XVI	XVII
		Distances, Å			
1–2	2.039	2.036	4–5	2.053	2.052
1–14	2.050	2.051	5–6	2.052	2.052
2–3	2.036	2.038	6–7	2.051	2.053
3–4	2.051	2.050	7–8	2.050	2.051
		Angles, Deg			
2–1–14	105.4	105.3	1–2–3–4	98.7	117.2
1–2–3	111.8	112.1	2–1–14–13	101.9	86.3
2–3–4	105.3	105.2	2–3–4–5	85.5	100.2
3–4–5	108.5	107.8	3–2–1–14	118.1	100.1
4–5–6	109.6	112.0	3–4–5–6	118.5	103.6
5–6–7	112.1	109.7	4–5–6–7	111.1	111.7
6–7–8	107.7	108.5	5–6–7–8	102.8	118.0

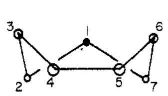
	cyclo-Hexadecasulfur			*cyclo*-Hexadecasulfur	
	XVIII	XIX		XVIII	XIX
		Distances, Å			
1–2	2.047	2.056	3–4	2.058	2.055
2–3		2.052			
		Angles, Deg			
2–1–16	103.6	104.9	3–2–1–16	115.2	118.5
1–2–3	111.7	105.1	1–2–3–4		102.2
2–3–4		106.5	2–3–4–5	79.2	29.7

	cyclo-Octadecasulfur		
	XX	XXI	XXII
	Distances, Å		
1–2	2.050	2.048	2.050
2–3	2.050	2.047	2.050
3–4	2.050	2.049	2.050
4–5	2.050	2.048	2.048
5–6		2.045	
6–7		2.052	
7–8		2.048	
8–9		2.051	
9–10	2.050	2.048	2.050
	Angles, Deg		
2–1–18	106.0	106.5	105.7
1–2–3	105.8	107.2	105.6
2–3–4	107.3	108.5	105.6
3–4–5	105.7	106.3	106.3
4–5–6	106.8	107.2	106.9
5–6–7		106.3	
6–7–8		107.5	
7–8–9		109.2	
8–9–10	106.0	107.7	105.7
18–1–2–3	97.1	102.2	94.1
1–2–3–4	85.1	88.2	93.3
2–3–4–5	87.3	81.6	83.3
3–4–5–6	84.0	72.7	90.1
4–5–6–7		87.7	
5–6–7–8		90.8	
6–7–8–9		104.7	
7–8–9–10		88.7	
8–9–10–11	98.7	107.0	94.7

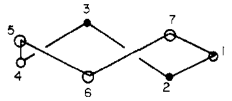
formation (D_{3d}) is the most stable and that a barrier of 23.3 kcal/mol separates it from the twist form (D_2) which has a relative energy of 15.1 kcal/mol. The twist–twist transformation goes through the boat (C_{2v}) as the transition state, which is 15.4 kcal/mol less stable than the chair. Our preliminary force field[13] gave a slightly larger estimate. Recent CNDO/2 calculations[26a] concluded that both the chair and the boat were stable conformations with the chair being only 4 kcal/mol more stable than the boat (the D_2 twist was not considered). However, the CNDO/2 results probably overestimate the effect of the d orbitals and underestimate nonbonded interactions as pointed out before.[14,27]

We employed ab initio molecular orbital calculations using a STO-3G basis set[28] to corroborate our force field results. This method has proven useful in structural studies of dimethyl disulfide,[14b] methyl ethyl disulfide,[14a] *cyclo*-octasulfur,[29] and numerous other molecules.[28] The minimum basis set is expected to give fairly reliable structural predictions without augmenting it with d functions.[30] The input geometries used for the ab initio calculations were the optimized structures from the molecular mechanics calculations. The boat, chair, and twist forms were examined. (The average CPU time required was 24 min per conformation, IBM 360/65, Gaussian 70 program.[31]) The chair form, the energy minimum (total energy −2359.0906 au), was calculated to be 14.2 kcal/mol more stable than the boat form, which is in good agreement with the value (15.4 kcal/mol) obtained from the molecular mechanics method. The twist form (D_2) was calculated to be more stable than the boat by 1.6 kcal/mol, being rather larger than the 0.3 kcal/mol value obtained from molecular mechanics. However, there is reasonable agreement between the ab initio and the molecular mechanics methods, both of which indicate that the boat is a transition state instead of a stable conformation, in contrast to what was suggested earlier.[26a] The bonding picture provided by the Mulliken population analysis of the STO-3G results is qualitatively the same as that discussed earlier[26a] from CNDO/2. No experimental findings exist with which the results of the calculations can be compared.

cyclo-**Heptasulfur.** This was the first known sulfur ring to contain an odd number of atoms,[4] which has been synthesized by Schmidt et al.[32] The substance forms pale yellow needles that rapidly decompose at room temperature. The twist-chair conformation of S_7 (IV) was calculated to be the most stable of several possible conformations, chair, boat, and twist-boat forms being respectively 0.3, 10.4, and 19.8 kcal/mol less stable. It is also interesting to note that the small energy difference between the chair (III) and the twist-chair (IV), which is mainly due to the eclipsing of S–S bonds, indicates that the S_7 chair conformation is quite flexible, undergoing an unhindered or slightly hindered pseudorotation. The calculated structures for the chair and twist-chair forms are given in Table III.



III, C_s

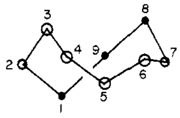


IV, C_2

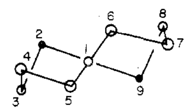
A low-temperature x-ray study[33] indicated that S_7 exists in a "chair" conformation; however, the reported *R* factor was as high as 20.9%. Our calculated results do not necessarily conflict with the x-ray data, since the chair is rather flexible and crystal packing forces may determine its configuration.

cyclo-**Octasulfur.** This is the most common allotrope of sulfur and the orthorhombic (α-S_8) crystalline modification[6] is the most stable form. The x-ray crystallographic structure determination[6] of α-S_8 has been reported by several groups of workers and the crown form has been found; this is in sharp contrast to cyclooctane, where the chair–boat conformation is the most stable. This difference is primarily due to the difference in the torsional energy functions of the molecules: threefold for cyclooctane and twofold for sulfur. Two other crystalline modifications of sulfur, monoclinic β-S_8[34] and γ-S_8,[35] have been reported, and the crown is also found in each case, with structural details being quite similar to those found in α-S_8. We calculated the symmetric crown (D_{4d}) to be the most stable, being more stable than the boat–chair by 10.3 kcal/mol mainly due to torsional strain. The twist-crown form where the dihedral angles have been twisted randomly by about 1° is only 0.08 kcal/mol less stable than the regular crown form. Thus the crown is rather flexible, which explains why it is slightly distorted in the crystal. An ab initio STO-3G investigation[29] also showed that the symmetric D_{4d} configuration is the energy minimum.

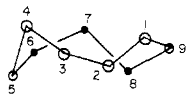
cyclo-**Nonasulfur.** A second known ring compound containing an odd number of sulfur atoms has been synthesized from the titanium–sulfur ring and dichlorotetrasulfane.[4,36] Its stability is about the same as that of S_6.[4,36] No structural details are known for S_9. We have investigated several possible conformers of S_9 and have found V to have the lowest energy. This conformation does not possess symmetry. Conformation VI has C_2 symmetry and a relative energy of 4.0 kcal/mol. Another symmetrical conformation (VII, with D_3) is much less stable (17.7 kcal/mol). The ranges of bond lengths, bond angles, and dihedral angles in I are respectively 2.047–2.054 Å, 103.1–107.6°, and 67.1–112.1°. (Structural details are given in Table III.)



V, C_1

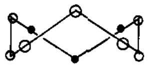


VI, C_2

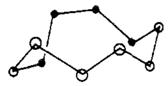


VII, D_3

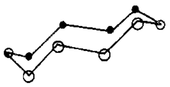
cyclo-**Decasulfur.** Several possible conformations (VIII–X) of S_{10} have been examined, and X was found to be the most stable, with less energy than VIII and IX by 7.3 and 7.8 kcal/mol, respectively. The conformation X has rather uniform bond lengths, bond angles, and dihedral angles, being respectively 2.044 Å, 109.2°, and 115.5°. Tuinstra[37] also concluded through geometric considerations that X is the most likely conformation.



VIII, C_{2h}

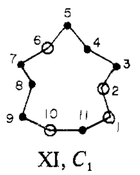


IX, C_1



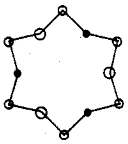
X, D_{5d}

cyclo-**Undecasulfur.** This compound has been synthesized from a reaction analogous to that used for S_9 with S_6Cl_2 being used instead of S_4Cl_2.[4] Its stability is similar to that of S_9, and it can be kept only in the dark at low temperature. Its structure is calculated to be the one shown by XI. Bond lengths vary from 2.046 to 2.053 Å, and bond angles, from 104.6 to 109.3°. Dihedral angles are usually in the range of 62–93° except one with 150° (Table III).

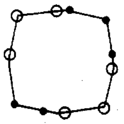


XI, C_1

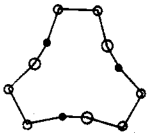
cyclo-**Dodecasulfur.** This was the first new sulfur modification ever synthesized.[38] Contrary to Pauling's prediction,[24] this substance, which crystallizes as pale yellow needles, is disconcertingly stable. This is in accord with the calculated strain energy (the steric energy in Table II). An x-ray structure analysis showed the highly symmetric form (XII, D_{3d}), in which the atoms are arranged in three planes with six in the middle plane and three each symmetrically above and below it. Thus, S_{12} is the smallest ring so far with a regular alternating cis–trans arrangement. Our calculated structure for the most stable conformation is in good agreement with the experimental one (Table I). We have also examined the conformations with point symmetries C_{2v}, D_3, and D_4 and have found that all of these conformations are less stable than the D_{3d} form by at least 27 kcal/mol, mainly due to torsional strain.



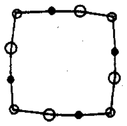
XII, D_{3d}



XIII, C_{2v}

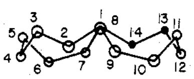


XIV, D_{3d}

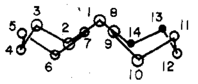


XV, D_4

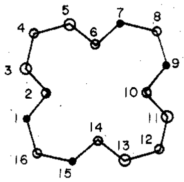
Larger *cyclo*-Sulfurs. There is nothing known experimentally about the structures of *cyclo*-tetradecasulfur (S_{14}) and *cyclo*-hexadecasulfur (S_{16}). It is interesting to note that our calculations based on bond energies (vide infra) predict that they are as stable (in terms of their enthalpy) as S_6 or S_9. Two possible conformations of S_{14} (XVI, XVII), both with C_2 symmetry, have been examined and found to be of about equal energy. Two possible conformations of S_{16}, one with symmetry C_{2v} (XVIII) and one with symmetry D_4 (XIX), have been examined. Conformation XVIII is calculated to be more stable than XIX by 14.6 kcal/mol. Two different conformations of *cyclo*-octadecasulfur (S_{18})[8,39] have been found in two different intramolecular allotropes, α-S_{18} and β-S_{18}. Their interesting structures have been elucidated quite recently. Bond lengths, bond angles, and dihedral angles in both conformations are quite similar to those in S_8 and S_{12}, except that there are certain extremely long bonds (2.1 Å) found in both cases. These long bonds are unexpected since torsional angles are rather normal in these molecules. Our calculations show that α-S_{18} has C_{2h} symmetry (which was erroneously assigned as C_{2v} in ref 8b) and β-S_{18} has C_i symmetry (see XX and XXI). Our calculated structures agree quite reasonably with the experimental ones (Table I) except for the extremely long bond lengths. However, the accuracy of experimental results may be responsible for the differences. The calculated energy difference between α-S_{18} and β-S_{18} is small (4.4 kcal/mol), with α-S_{18} being more stable; this is what would be expected from the model study. It is very interesting to note that conformation XXII (C_{2h}) has a stability between those of α-S_{18} and β-S_{18}, namely, only 1.3 kcal/mol less stable than α-S_{18}. Conformation XXII differs from XX only by the spatial arrangement along 1–18 and 9–10 bonds. Thus, the molecular halves are nearly identical, and their energy difference is therefore essentially from van der Waals interactions. The synthesis and isolation of XXII should offer a challenge to experimental sulfur chemists.



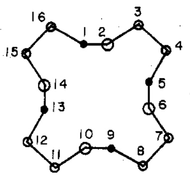
XVI, C_2



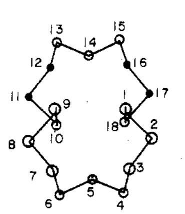
XVII, C_2



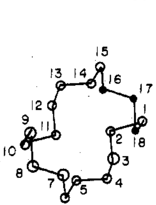
XVIII, C_{2v}



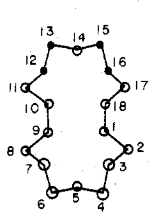
XIX, D_4



XX, C_{2h}



XXI, C_i



XXII, C_{2h}

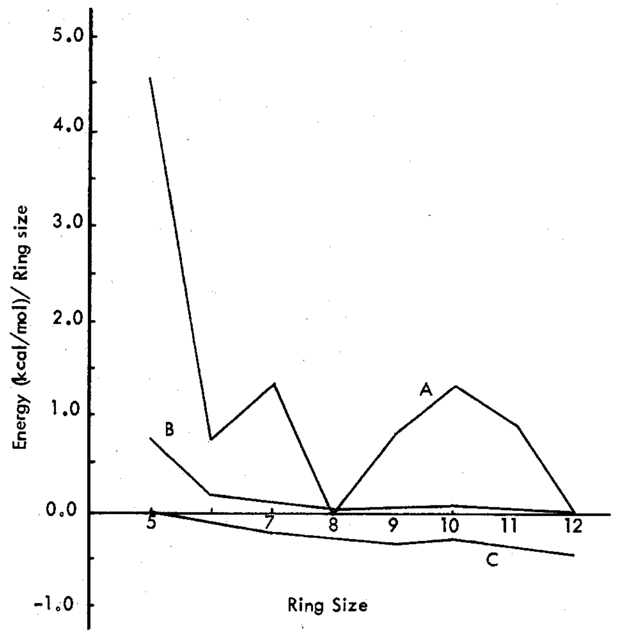
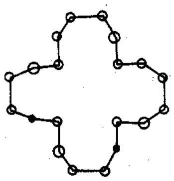
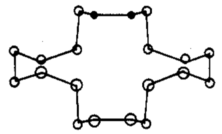


Figure 1. Partition of the total steric energies in the S_5 to S_{12} rings: curve A, torsional + torsional-bend energies; curve B, bending + stretch-bend energies; curve C, van der Waals energies. Stretching energies are very small (near zero) and are not shown here.

cyclo-Icosasulfur (S_{20}), like S_{18}, contains complicated motifs. Our calculated structure is in good agreement with the experimental one; the comparison is shown in Table I. The most stable conformation is the one with C_2 symmetry (XXIII). The conformation with D_2 symmetry, which has the same trans–cis arrangement as XXIII but with two more C_2 axes, was calculated to be 0.8 kcal/mol less stable than XXIII. The conformer with C_{2h} symmetry (XXIV) is 19 kcal/mol less stable than the C_2 form due to eclipsing of S–S bonds found in the former conformation.



XXIII, D_2



XXIV, C_{2h}

Steric Energies, Enthalpies, and Bond Energies

Steric Energies. The calculated steric energy as well as the steric energy with respect to ring size (the steric energy per sulfur atom of the ring) is given in Table II. The present calculation also allows us to see how the steric energy is partitioned among the internal degrees of freedom. The partition (S_5 to S_{12}) is shown in Figure 1. As can be seen from Figure 1, the steric energy per sulfur passes through a minimum at S_8 and through a maximum at S_7. It is quite obvious that the torsional strain is the predominant portion of the total steric energy. The conformational difference between the carbocyclic and the sulfur rings can be fully appreciated by comparing Figure 1 with the corresponding figure for carbocyclic rings.[40]

Enthalpies. The heats of formation of these molecules may be calculated as

$$\Delta H_f^\circ(g) = N_{SS}X_{SS} + \text{PTF} + E_s \qquad (1)$$

where E_s is the steric energy of the molecule calculated by our program, N_{SS} is the number of S–S bonds, X_{SS} is the energy parameter associated with N_{SS}, and PTF is the partition function contribution. Usually it has the value 2.4 kcal/mol from translational and rotational contributions and a correction for constant pressure. Torsional contributions are neglected, since the barriers are pretty high. The enthalpy increase due to the admixture of a higher energy conformation needs to be allowed for in the case of S_{18}. The use of only a single X term here is due to interdependence of bond energy parameters.[41] We choose the heat of formation of S_8(g) (24.32 kcal/mol, equal to the heat of sublimation)[42] as the standard to find the only parameter X_{SS} in eq 1. The calculated enthalpies are shown in Table II.

The experimental heats of formation for S_6 and S_8 are probably more accurate than others.[42] The calculated enthalpy of S_6 is 24.79 kcal/mol which is in good agreement with the experimental value,[42] 24.36 kcal/mol. However, the calculated enthalpies for S_7 and S_5, 31.38 and 43.51 kcal/mol, respectively, are too high when compared with experimental estimates,[42] 27.17 and 26.14 kcal/mol. The experimental enthalpy for S_7 is probably too small since from the thermal stability and theoretical viewpoint it should be less stable than the S_6. Even larger experimental errors in S_5 would be expected, since it is only a minor constituent in the vapor, the properties of which are not very well defined and the existence of which is even doubted by some people.[43] We feel that our calculated values are probably more reliable than the experimental ones.

Bond Energies. As defined,[44] bond energies for elemental compounds are taken as the heats of atomization or the negative of the binding energy divided by the number of bonds. The heats of atomization are calculated as

$$\Delta H_a^\circ(g) = 65.65N_S - \Delta H_f^\circ(g) \qquad (2)$$

where the first term on the right-hand side is the conversion factor from ΔH_f° to ΔH_a° and N_S is the number of S atoms in the molecule. The coefficient 65.65 is the heat of formation of gaseous sulfur atoms in their ground state at 298.15 K from the element in its standard state.[44] The bond energy obtained this way for elemental sulfur is often called *apparent bond energy*.[45] Our calculated values are shown in Table II.

The experimental bond energy difference between S_8 and S_6 is quite well reproduced. The difference between S_8 and S_{12} is calculated to be quite small, as expected from their identical stretching force constants and thermal stabilities.[43] Similar bond energies are also found in S_{18} and S_{20}. Therefore, the S–S bond is strongest in S_8, S_{12}, S_{18}, and S_{20} and next strongest in the remaining molecules except S_5. The latter, if it can be synthesized, would be very reactive due to its strain. The average bond strength is thus about 62 kcal/mol, depending on the molecule, which takes third place among all homonuclear single bonds exceeded only by H–H and C–C.

Conclusion

The present study proposes a theoretical method for the calculation of structures, energies, and enthalpies of elemental sulfur. It can easily be extended to almost any known or imagined homologue or conformation. Its reliability is evidenced by the agreement between the calculated and experimental results where the latter exist. Predictions have been made in some cases where experimental results do not now exist. The predictions suggest that many more structures are possible than those presently known to exist and offer a challenge to experimental chemists.

Registry No. S_4, 19269-85-3; S_5, 12597-10-3; S_6, 13798-23-7; S_7, 21459-04-1; S_8, 10544-50-0; S_9, 18808-47-4; S_{10}, 14721-09-6; S_{11}, 60349-28-2; S_{12}, 14999-38-3; S_{14}, 60349-29-3; S_{16}, 60349-30-6; S_{18}, 41371-12-4; S_{20}, 42817-30-1; S, 7704-34-9.

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Contribution from the Department of Chemistry,
University of Vermont, Burlington, Vermont 05401

Electrochemistry of the Nitroprusside Ion in Nonaqueous Solvents

WILLIAM L. BOWDEN, PETER BONNAR, DAVID B. BROWN,* and WILLIAM E. GEIGER, Jr.*

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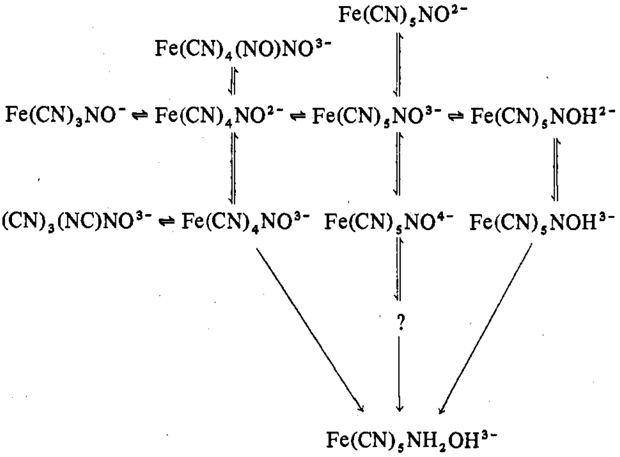
The electrochemical reduction of the pentacyanonitrosylferrate(II) anion has been studied in nonaqueous aprotic media by polarography, cyclic voltammetry, and coulometry. In contrast to results from aqueous solution, the initial one-electron reduction proceeds with a rapid loss of cyanide to give the blue five-coordinate tetracyanonitrosylferrate(I) anion. The tetracyanonitrosylferrate(I) anion undergoes a further reversible reduction and an oxidation which is reversible at fast sweep rates.

In recent years the chemistry, particularly the redox chemistry, of the nitroprusside ion, $Fe(CN)_5NO^{2-}$, has been the subject of widespread interest,[1–3] and the reduction processes have been studied by a variety of synthetic[4–7] and physical techniques, including EPR,[8–16] Mössbauer spectroscopy,[17] and crystallographic[18] and thermoanalytical[16] methods. These studies have demonstrated that there exist at least two products resulting from the one-electron reduction of $Fe(CN)_5NO^{2-}$, one blue and the other yellow-brown. There is disagreement in the literature as to the identity of these species, and among the formulations which have been proposed for the products of the one-electron reduction of $Fe(CN)_5NO^{2-}$ are $Fe(CN)_5NO^{3-}$, $Fe(CN_5NOH^{2-}$, $Fe(CN)_4NO^{2-}$, $Fe(CN)_5NO_2{}^{5-}$, $Fe(CN)_4(NC)NO^{3-}$, and $Fe_2(CN)_{10}{}^{6-}$. Most of the discussion has centered on the first two, with conflicting claims for their assignment to the blue or brown species. The electrochemical reduction of the nitroprusside ion in aqueous media has been investigated by several groups,[19–24] most recently by Masek and co-workers.[22–24] The latter studied the nitroprusside problem by a variety of electrochemical techniques, including polarography, cyclic voltammetry, and coulometry. Rather complex behavior was encountered in these investigations, wherein two successive reversible reductions at −0.36 and ∼−0.6 V were followed by an irreversible multielectron reduction at ∼−0.9 V. Whereas the total current was equivalent to the transfer of 4 e, only the initial reduction appeared to be a clean, well-behaved reduction process. To rationalize the results of these studies, a reduction sequence was proposed (Scheme I[24]). Characterization of the initial reduction process is of particular interest, since the products formed are those which have been examined by EPR and Mössbauer and electronic spectroscopy.

The species $Fe(CN)_5NO^{3-}$, $Fe(CN)_5NOH^{2-}$, and $Fe(CN)_4NO^{2-}$ are of interest as the species which have been proposed as the brown and blue nitroprusside reduction products. The complex reduction mechanism of nitroprusside in aqueous solution prompted the present investigation of the nonaqueous electrochemical behavior of this system, since the protonated product, $Fe(CN)_5NOH^{2-}$, is not expected to form in aprotic media. Tetraalkylammonium salts of the nitroprusside ion are soluble in a variety of nonaqueous solvents, including acetonitrile and dichloromethane, and the electrochemical behavior of the nitroprusside ion has been studied in these solvents using polarography, cyclic voltammetry, and exhaustive electrolysis at controlled potential. The results of these studies, supported by EPR and electronic spectroscopy, have elucidated some details of the reduction chemistry of the nitroprusside ion in nonaqueous solutions and are reported in this paper.

Scheme I. Reduction Scheme for Nitroprusside Ion in Aqueous Solutions[24]



Experimental Section

Tetra-*n*-butylammonium nitroprusside, $[N(C_4H_9)_4]_2Fe(CN)_5NO$, was prepared by metathesis of sodium nitroprusside with tetrabutylammonium bromide in water and was purified by recrystallizations from water. The tetrabutylammonium hexafluorophosphate, $N(C_4H_9)_4PF_6$, was purified by repeated recrystallizations from hot ethanol and was used throughout as the supporting electrolyte (0.1 M).

Electrochemical measurements were taken with a PAR 173 potentiostat in conjunction with a Hewlett-Packard 3300A function generator and recorded on a Hewlett-Packard 7001A X-Y recorder or a Tektronix 502A dual-beam oscilloscope equipped with a C-27 camera.

All experiments were carried out in solutions deoxygenated with nitrogen. Dichloromethane was distilled from CaH_2 under nitrogen immediately before use. Eastman Spectrograde acetonitrile was used without further purification. Bulk electrolyses were carried out in a normal three-compartment cell using a mercury pool working electrode with a platinum gauze auxiliary electrode. All potentials are given relative to the aqueous saturated calomel electrode. Bulk electrolyses were considered complete when the limiting current