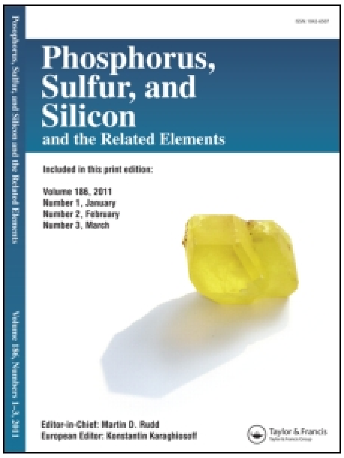

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Garcia-fernandez, H. , Coudanne, H. and Pindat, M. A.(1989) 'Derivatives of Cyclic Inorganic Sulfur Imides', Phosphorus, Sulfur, and Silicon and the Related Elements, 41: 3, 405 — 417
To link to this Article: DOI: 10.1080/10426508908039731
URL: http://dx.doi.org/10.1080/10426508908039731

Phosphorus, Sulfur and Silica, Vol. 41, pp. 405–417
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DERIVATIVES OF CYCLIC INORGANIC SULFUR IMIDES

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Abstract 1) Cyclic inorganic sulfur imides, S_7NH, $S_6(NH)_2$ 1.3 $S_5(NH)_3$1.3.5 and $S_4(NH)_4$1.3.5.7. in solution in polar solvents (acetone, acetonitrile, etc.) release the radicals S_7N-, $S_6N_2^{2-}$ and S_5N^{3-} under the action of alkali. Their study by near UV spectroscopy reveals unstable radicals which rapidly pass into the more stable S_4N^- radical. The latter in turn gives, by charge transfer with the solvent (acetone), the blue complex $[S_4N\text{--}OC(CH_3)_2]$. Non polar solvents ($CCl_4$) do not give this charge transfer complex (C.T.C.).

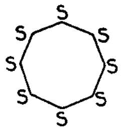
2) The sulfur imides mentioned above react with a solution of S_8 to give, via hydrogen bonds, crystalline C.T.C's of formula $[3\ S_8\text{---}S_7NH.]$ or $[2\ S_8\text{---}S_6(NH)_2 1.3]$. X-ray examination reveals that these complexes are isotypes of the sulfurs $S_8\beta$ and $S_8\gamma$ whose crystals are stabilized by intermolecular hydrogen bonds.

3) The reaction of the sulfur imides with formic aldehyde gives primary cyclic polyalcohols, such as $S_5(N\text{-}CH_2OH)_3$ or $S_4(N\text{-}CH_2OH)_4$, which form typical molecular cages through intramolecular hydrogen bonds.

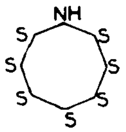
4) Examination of Van der Waals bonds of the crystallized sulfur imides enables their comparison with molecules of these compounds containing other types of bonds.

INTRODUCTION

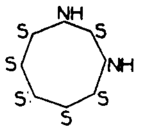
We have isolated four sulfur imides with eight-membered rings which theoretically result from the progressive replacement of sulfur atoms by NH groups in the S_8 ring leading to the four imides:



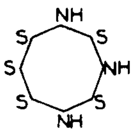
S_8



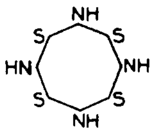
S_7NH



$S_6(NH)_2$



$S_5(NH)_3$



$S_4(NH)_4$

In addition to these four sulfur imides, the three isomers, $S_6(NH)_2 1.4$, $S_6(NH)_2 1.5$, $S_5(NH)_3 1.3.6$, have been isolated which makes a total of seven sulfur imides whose structure and chemical properties have been determined by radiocrystallography.

Sulfur imides are insoluble in water but soluble in organic solvents. However, a fundamental distinction is to be made whether the organic solvent is polar or non polar. Non-polar solvents have a restricted action and only cause an initial dissociation of the type:

$$S_7NH \rightleftarrows S_7N^- + H^+$$

INFLUENCE OF THE SOLVENT ON THE UV SPECTRUM OF SULFUR IMIDES

Solutions of sulfur imides in typical non-polar solvents such as carbon tetrachloride reveal, on examination of their UV and visible spectra, a very weak dissociation which is shown by two very close weak bands at 260 and 280 nm (Figure 1, (1 and 2)), (Figure 2 (3 and 4)). In the four imides, S_7NH, $S_6(NH)_2$, $S_5(NH)_3$ and $S_4(NH)_4$, the band at 260 nm is more pronounced than that near 280 nm. These solutions in CCl_4 give, in the presence of an alkali (KOH), a UV spectrum in which the absorption bands at 260 and 280 nm significantly increase in intensity, probably owing to a stronger dissociation of the sulfur imides (Figure 1 (1'.2'), (Figure 2 (3'.4'). Moreover, the ratio of the relative intensities of the bands at 260 and 280 nm differs in the spectra of the four imides, thus permitting their differentiation. For S_7NH, the band at 280 nm becomes tenfold more intense than that at

260 nm. The same is observed for $S_6(NH)_2$, but here the band at 280 nm is only 3 to 4 times as intense as the one at 260 nm. $S_5(NH)_3$ shows two bands of about the same intensity and, for $S_4(NH)_4$, the band at 260 nm is more intense than that at 280 nm. In solutions of sulfur imides in a polar solvent such as acetone, the absorption bands in the ultraviolet region are shifted by the solvent towards longer wavelengths and lie at 314 and 328 nm (Figure 3). The greater power of dissociation of this solvent also permits a direct differentiation of the four spectra without using an alkaline reagent. For S_7NH, the band at 328 nm is much more intense than at 314 nm; for $S_6(NH)_2$, the UV spectrum shows a band at 328 nm which is only 3 to 4 times as intense as the band at 324 nm. In the spectrum of $S_5(NH)_3$, the two bands have about the same intensity and for $S_4(NH)_4$ the band at 314 nm is more pronounced than at 328 nm.

FIGURE 1

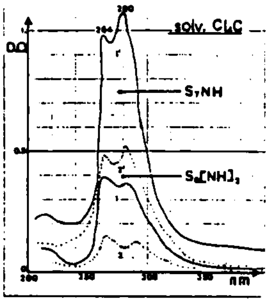


FIGURE 2

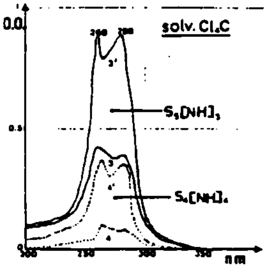
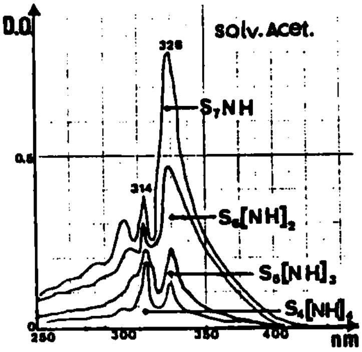


FIGURE 3



The solutions of sulfur imides in acetone release the corresponding radicals, S_7N^-, $S_6N_2^{2-}$, $S_5N_3^{3-}$ and $S_4N_4^{4-}$, under the action of an alkaline reagent. Examination of the UV and visible spectra reveals that these radicals are highly metastable in an alkaline medium and in the presence of a polar solvent and pass quite rapidly into the more stable radical S_4N^-. The latter gives, by charge transfer with the solvent molecules, a charge transfer complex (C.T.C.) which shows a dark blue colour and whose absorption band lies at 585 nm in the visible region: $[S_4N^- \text{---} OC(CH_3)_2]$. This C.T.C. remains stable for some time, but it is photosensitive and loses its colour progressively through photolysis (Figure 4) to become practically colourless after several hours. This is a characteristic of this C.T.C. This colouration has been erroneously imputed in the literature to the radical-ions released. In fact, the radicals mentioned above are practically colourless and have their own absorption bands in the UV region (when in the presence of a non-polar solvent). However, in the presence of a polar solvent (acetone, acetonitrile, etc.), they react with the solvent, as indicated, and give the corresponding coloured C.T.C.

The transformation of the radical-ions, S_7N^-, $S_6N_2^{2-}$ and $S_5N_3^{3-}$, into the common radical S_4N^- results from a dismutation, as it occurs in sulfur solutions placed in an alkaline medium (here liquid ammonia). This has been studied by Bernard, Lelieur and Lepoutre[1] and shows that in the sulfur molecule S_8, sulfur is partly oxidised as S_4N^- and partly reduced according to the equation:

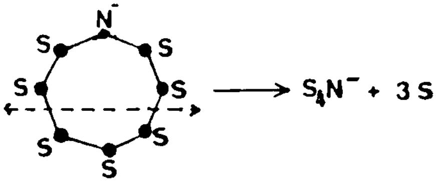
$$5/4\ S_8 + 4\ NH_3 \longrightarrow S_4N^- + S_6^{2-} + 3\ NH_4^+$$

The same mechanism might logically explain the dismutation of the radical-ion S_7N^- released by alkali as follows:

$$S_7N^- \rightleftarrows 3/8\ S_8 + S_4N^-$$

The radical S_4N^- then reacts with the polar solvent to give the dark blue C.T.C.

Chivers and Fielding[2] have isolated the complex {*t*-Bu_4N^+---S_4N^-} in the crystalline state and have shown that the structure of S_4N^- is an open-chain structure, $[S=S-N=S=S]^-$. The transformation of the ring S_7N^- (in the presence of an alkali) into the ion S_4N^- can also be explained by a ring division according to the scheme:



For the radicals $S_6N_2^{2-}$ and $S_5N_3^{3-}$ a dismutation is more difficult to explain unless we admit that a liberation of nitrogen occurs.[1]

$$2\ S_6N_2^{2-} \rightleftharpoons 2\ S_4N^- + 3\ S^{2-} + N_2 \uparrow$$

$$2\ S_5N_3^{3-} \rightleftharpoons 2\ S_4N^- + 2\ S^{2-} + 2\ N_2 \uparrow$$

Under the same conditions, $S_4N_4^{4-}$ does not give any coloured reaction, suggesting the absence of dismutation. This is probably due to a maximum rate of oxidation of sulfur in this ring (+4) which prevents dismutation.

The blue complex $[S_4N{-}{-}{-}OC(CH_3)_2]$ does not form instantaneously but passes first through a transitory stage which lasts a few seconds. At the very beginning of the reaction, one can observe weak bands at about 470 nm which probably correspond to the radicals, $S_5N_3^{3-}$, S_7N^- and $S_6N_2^{2-}$ (before dismutation). These bands disappear rapidly, after 4-5 seconds (Figure 5), to the benefit of the band at 585 nm which has its maximum intensity during the same period of time (Figure 4).

FIGURE 4

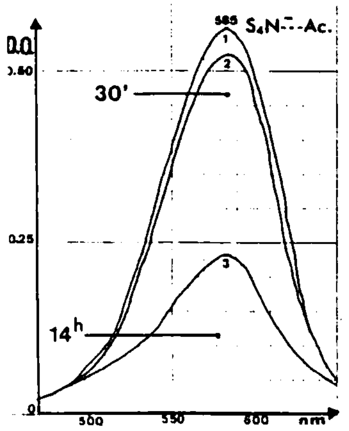
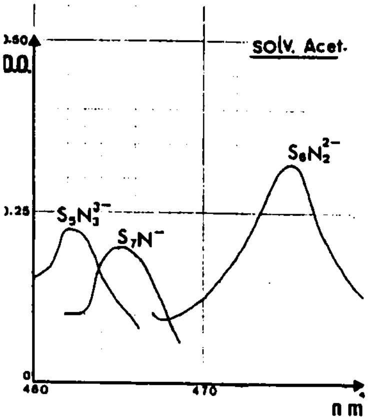


FIGURE 5



THE CHARGE TRANSFER COMPLEXES (C.T.C.'S) [S_8---sulfur imides]

In recent years the notion of charge transfer complexes covers both the notion of hydrogen bonding and of an electron donor acceptor complex (E.D.A. complex). After the study of solutions, solids are now being extensively studied for about the last twenty years. The heats of formation of these complexes are of the order of 1 to 10 kcal/mol and the intermolecular distances are of the order of 2.8 to 3.5 Å. The relative stability of the complex results from the fact that an electron can be transferred from a donor molecule (D) to an acceptor molecule (A). The C.T.C. can be represented as follows:

$$\dot{A} + \ddot{D} \longrightarrow [\ddot{A}{-}{-}{-}\dot{D}] \rightleftarrows \ddot{A}^{-} + \dot{D}^{+}$$

C.T.C. ionic

The bond in these complexes results from attractive forces between molecules which are poor in electrons (A) and molecules which are rich in electrons (D). Huyskens[4] has reported the fundamental importance in solutions and also in solids of the interatomic and intermolecular distances:

$$\begin{array}{ccccccc|ccccc}
A & + & D & + & D & \longrightarrow & A\text{--} & \text{-}D & \rightleftarrows & \overset{-}{A} & + & D \\
a\text{-}p & & & & d & & a\text{-}p & d & & & & r^{o}p^{+}\text{-}d \\
r^{o}ap & & & & r^{o}dp & & r^{o}ap & rpd & & & &
\end{array}$$

These distances have been determined by X-ray diffraction and IR and Raman spectroscopy.

C.T.C.'s are thus defined by the relation:

$$mA + nb \longrightarrow A_m^{-p}\text{---}D_n^{+p}$$

where p is the charge transfer rate between A and D.

Weak intermolecular reactions give a complex whose fundamental state is essentially neutral, $p = 0$. For not very strong interactions, i.e., for $p < 1$, the state is partially ionic, as in the C.T.C.'s, and for very strong interactions, the state is fundamentally ionic, $p = 1$, as in ordinary ionic compounds. This permits us to define various types of crystals: (1) molecular crystals (non-conducting), $p = 0$; (2) C.T.C. crystals (with hydrogen bonding or E.D.A. bonding), $p < 1$; and (3) ionic crystals, $p = 1$. C.T.C. crystals with a mixed valence state have been discovered recently. These solids conduct, for example, the complex, [TTF---TCNQ]. Such complexes are called "organic metals".[5]

VAN DER WAALS BONDS IN MOLECULAR CRYSTALS

Octahedral sulfur S_8 is a classical example of an isolated molecular crystal, $p = 0$. The bonds between the rings S_8 in the crystal are weak and of the van der Waals type ($\varepsilon = 1$ to 2 kcal/mol and $d = 3.5$ to 4.0 Å).

There exists several well-known crystalline varieties of elemental sulfur S_8. The earliest known and also the only stable one at room temperature is the orthorhombic form or α-sulfur. The other two forms β and γ are monoclinic and metastable at room temperature. They pass spontaneously and rapidly into the α-form.

The structural pattern is the same in the three crystalline forms, α, β, and γ. The more compact form is α-sulfur. It has an orthorhombic unit cell with Fddd symmetry containing 16 S_8 rings. β-Sulfur (or Mitscherlich sulfur) has a monoclinic unit cell, $P2_1/c$, and contains 6 S_8 rings. γ-Sulfur (or Gernez sulfur) has a monoclinic unit cell, P2/n, with 4 S_8 rings. The intermolecular distances in the three forms are all between 3.62 and 4.00 Å. The bonds are therefore van der Waals bonds.

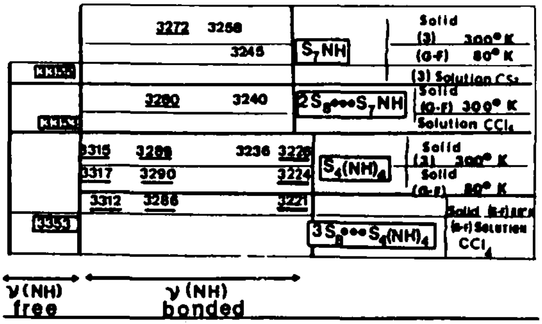
The transformation of the β and γ forms into the α form occurs spontaneously at room temperature with emission of heat:

$$S_8\beta \longrightarrow S_8\alpha \; + \; 2.81 \text{ cal/g}$$

HYDROGEN BONDS IN CRYSTALS OF SULFUR IMIDES

Study by radiocrystallography permits us to determine the unit cell and the structure of sulfur imides in the crystalline state but not to distinguish the sulfur atoms clearly from the NH grouping. Infrared and Raman vibrational spectra show immediately, however, the NH vibrations (νNH)[6] and reveal, moreover, whether NH is free (νNH at about 3335 cm^{-1}) or bonded by a hydrogen bond (νNH at about 3300-3200 cm^{-1}), as indicated in the table (Figure 6) for solutions in CCl_4.

FIGURE 6



Free ν(NH) is observed near 3335 cm^{-1}. The molecules of sulfur imides are not associated in the solvent. Bonded ν(NH) are observed in the crystals and are shifted towards lower frequencies, thus confirming the presence of intermolecular hydrogen bonds in the crystals. The presence of several components between 3200 and 3300 cm^{-1} however remains to be explained. The most plausible explanation is a possible perturbation of the NH grouping by the free sulfur orbitals.

In the series of sulfur imides the melting points increase with the number of NH groups and, therefore, with the number of intermolecular hydrogen bonds.

	P.F.
S_8 (only van der Waals bonds)	112.0°C
S_7NH	113.5°C
$S_6(NH)_2$1.3	125.5°C
$S_5(NH)_3$1.3.5	130.0°C
$S_4(NH)_4$1.3.5.7	145.0°C

The preponderant role of <u>intermolecular hydrogen bonds</u> is particularly manifest in the complexes of [sulfur---sulfur imides]. Solution of sulfur imides indeed react with sulfur to give, after evaporation of the solvent, crystals with an elongated hexagonal shape and with formulae:

2 S_8---S_7NH		3 S_8---S_7NH
2 S_8---$S_6(NH)_2$1.3		3 S_8---$S_6(NH)_2$1.3
2 S_8---$S_5(NH)_3$1.3.5	or	3 S_8---$S_5(NH)_3$1.3.5
2 S_8---$S_4(NH)_4$1.3.5.7		3 S_8---$S_4(NH)_4$1.3.5.7

All these molecular associations occur through intermolecular hydrogen bonds. They have a well-defined formula and, like the chemical species, the sulfur to sulfur imide ratios are stoichiometric.

X-ray diffraction examination reveals that the unit cell of the crystals of these associations containing two S_8 rings with one ring of sulfur imide has the same symmetry $P2_1/c$ and the same dimensions as that of monoclinic β-S_8 (or Gernez sulfur). Similarly, the crystalline unit cell of the association of 3 S_8 rings with 1 ring of sulfur imide has the same symmetry P2/n and the same dimensions as the unit cell of γ-S_8 (or Mitscherlich sulfur). This seems to suggest that they result from the replacement, in the unit cell of β-S_8 or of γ-S_8, of a S_8 ring by a corresponding imide ring.[7,8]

It is most likely that the intermolecular hydrogen bonds have a stabilizing effect on the new crystal structure since the two unit cells of the monoclinic β- and γ-sulfurs are metastable at room temperature, while the complexes [sulfur---sulfur imide] are remarkably stable. Moreover, a charge transfer NH---S_8 is manifest in the complex [$3S_8$---$S_4(NH)_4$] since the two components, when taken separately, are insoluble in solvents such as CCl_4, while the complex is highly soluble. This is one of the characteristics of the C.T.C.'s according to Mulliken's classical observations[9] and the work by Andrews and Keefer.[10]

These conclusions are summarized in Figure 7.

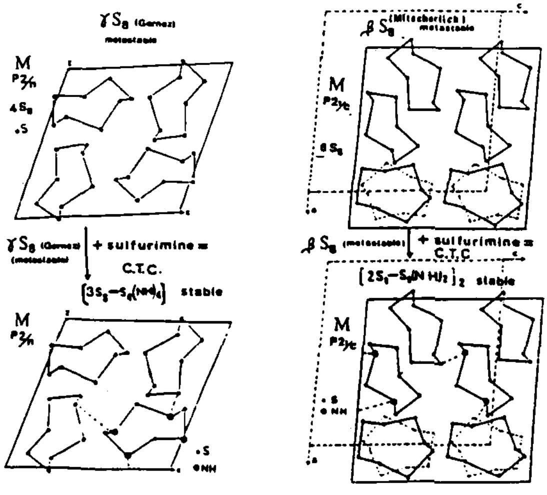
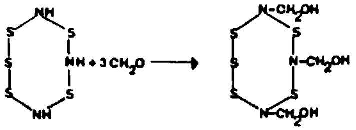


FIGURE 7

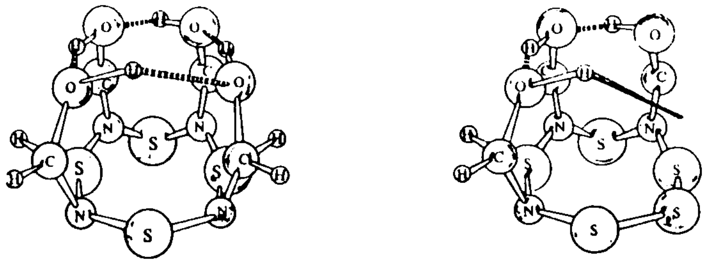
INTRAMOLECULAR HYDROGEN BONDS

In inorganic cyclic sulfur imides, the mobile hydrogen of the NH groups can be replaced by various radicals. For instance, the reaction with formic aldehyde, CH_2O, leads to primary cyclic polyalcohols.



Similarly, the alcohol $S_4(N\text{-}CH_2OH)_4$ can be prepared from the imide $S_4(NH)_4$. Study of a single crystal of these compounds by X-ray diffraction shows that the molecules have the conformation of molecular cages which are defined in space by 6 cyclic faces as in the compound $S_4(NCH_2OH)_4$. At the base of the cage there is a distorted ring S_4N_4 and at the top an O_4H_4 ring formed by four intramolecular hydrogen bonds.[11] The molecule of the trialcohol $S_5(N\text{-}CH_2OH)_3$1.3.5 has an open-cage structure with two intramolecular hydrogen bonds at its top and a third intermolecular bond with the alcohol grouping of the contiguous molecule in the crystal (Figure 8).[12]

FIGURE 8



$S_4(N\text{-}CH_2OH)_4$ $S_5(N\text{-}CH_2OH)_3$

THE FOUR TYPES OF BONDS IN THE CRYSTALLINE SULFUR IMIDES AND THEIR DERIVATIVES

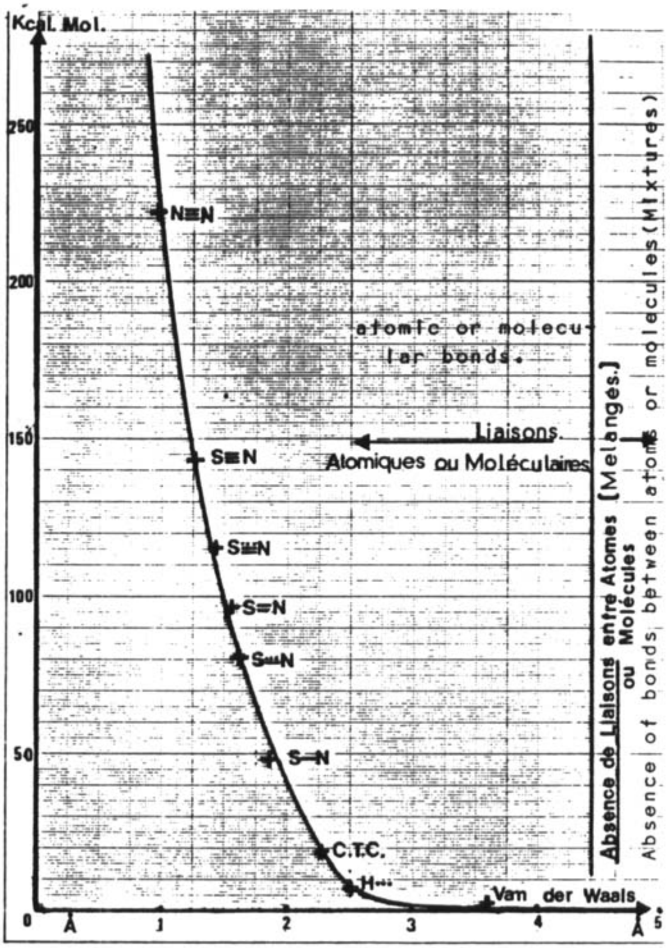
The various types of bonds described above can be classified arbitrarily in order of increasing energies.

Type of bond	Distance, Å	Energy, kcal/mol	Crystal Type	Compound (C.T.C.)
Van der Waals	3.5 to 4.0	< 2.0	molecular	sulfur (S_8)
Hydrogen	2.5 to 2.9	2.5 to 5.0	molecular	$[3S_8{-}{-}{-}S_7NH]$
C.T.C.	-2.5	1.7 to 10	molecular	$[3S_8{-}{-}{-}I_3CH]$
Ionic	2.0 to 2.4	50 to 70	ionic	$I^- - NH_4^+$

We also can classify the covalent bonds S-N in the molecules of sulfur imides in order of bond order corresponding to the bond energies and bond lengths. This leads to the curve shown in Figure 9. This curve represents a branch of a parabola and shows an analogy between the various types of bonds (molecular or atomic) in the sulfur imides. These various types of bonds are apparently of the same nature since one passes gradually from the weakest bonds, or van der Waals bonds, to the strongest ones, either molecular or atomic. This seems to support the present tendency to establish criteria for unification in the fields of physics and chemistry.

Covalent Bond	Distance, Å	Energy, kcal/mol	Bond Order	Compound	Ref.
S—N	1.740	48.27	1.0	H_2N-SO_3H	(13)
S╌N	1.670	69.30	1.4	$S_4(NH)_4$	(13)
S╍N	1.630	79.10	1.5	S_4N_4	(14)
S═N	1.540	98.20	2.0	$S_4N_4F_4$	(15)
S≣N	1.446	115.00	2.5	NS-F	(16)
S≡N	1.250	143.00	3.0	$S{\equiv}N^+$	(16)
N≡N	1.097	226.00	3.0	N≡N	(17)

FIGURE 9



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