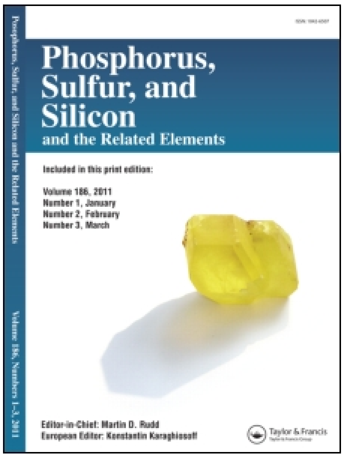

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INORGANIC HETEROCYCLE COMPOUNDS AND CHARGE TRANSFER COMPLEXES

H. Garcia-fernandez[a]
[a] Centre National de la Recherche Scientifique (CNRS), Laboratoire de Physico-Chimie des Materiaux, Meudon, France

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INORGANIC HETEROCYCLE COMPOUNDS AND CHARGE TRANSFER COMPLEXES

H. GARCIA-FERNANDEZ

Centre National de la Recherche Scientifique (CNRS), Laboratoire de Physico-Chimie des Materiaux, 1, Place A. Briand 92190 Meudon (France)

By reduction of sulfur nitride, S_4N_4, with hydrazine, N_2H_4, we have prepared all the seven eight-membered ring sulfurimines in the crystallized form. However, besides sulfurimine crystals, one notes the presence of *elongated hexagonal crystals*, which are very different in size and morphology.

A study of these isolated crystals by:

I. Chemical analysis.
II. Infrared spectrography and U.V. spectrography.
III. Radiocrystallography,

shows that they are molecular charge-transfer complexes (C.T.C.), Hydrogen bond type:

$$[\text{Cyclo } S_8] \rightarrow [\text{Cyclo(8)Sulfurimine}]$$

$$\underset{\text{Donor.}}{D.^+} \rightarrow \underset{\text{Acceptor.}}{A.^-}$$

A few examples are given in Figure 11, in which are reported the chemical, crystallographical and spectroscopic results for solid octahedral sulfur derivatives.

I. EIGHT-MEMBERED RING SULFURIMINES $S_{8-n}(NH)_n$

From the S_8 ring are theoretically derived 7 imines by progressive substitution of 1 to 4 NH groups for 1 to 4 non-adjacent sulfur atoms, which leads to the following series:

S_8	S_7NH	1,3-$S_6(NH)_2$	1,3,5-$S_5(NH)_3$	1,3,5,7-$S_4(NH)_4$
		1,4-$S_6(NY)_2$	1,3,6-$S_5(NH)_3$	
		1,5-$S_6(NH)_2$		

The first known imine is $S_4(NH)_4$. It was obtained by Wolbling in 1908 by reduction of the nitride S_4N_4 with stannous chloride in a methyl alcoholic solution by heating. By reduction with hydrazine (N_2H_4, H_2O) of a mixture of sulfur S_8 and of the nitride S_4N_4 in an inert solvent such as CCl_4, one obtains,[2] after reaction and evaporation of the solvent, an aggregate of crystals containing all 7 sulfurimines which are then isolated by chromatrography on activated silica gel or on polystyrene gel. The respective yields in % are reported in Figure 1.

Except for the 1,3,6-$S_5(NH)_3$ term, of which only the unit cell is known, the crystal and molecular structure of the other imines was determined by radiocrystallography and infrared spectrography.

Prior to separation by chromatography, one observes among the crystals of the different imines the presence of large crystals with hexagonal elongated facies, which are very different from those of the other imines (Figure 2).

A chemical analysis of these crystals shows that they are very poor in nitrogen (3.9%) and hydrogen (0.29%), but very rich in sulfur (95.8%), which should corre-

$S_4N_4 + S_8 + N_2H_4 \rightarrow$

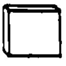
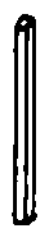
FORMULA	S_7NH	$S_6N_2H_2$ 1,3	$S_6N_2H_2$ 1,4	$S_6N_2H_2$ 1,5	$S_5N_3H_3$ 1,3,5	$S_5N_3H_3$ 1,3,6	$S_4N_4H_4$	S_8	$2\ S_8 \rightarrow S_6NH_2$
%	56,90 %	11,2	1,5	2,6	6,10	0,5	0,2	21,2	
FACIES									
Symmetry	Pnma O	Pbca O	$P2/_n$ M	Pnma O	Pnma O	O	Pnma O	Fddd O	$P2_1/_c$ M

FIGURE 1

spond to the elemental formula $S_{22}N_2H_2$. X-ray examination of these crystals reveals a monoclinic unit cell, $P2_1/c$, of formula: $[2S_8 \rightarrow S_6(NH)_2]_2$. Consequently, two S_8 rings are associated with one $S_6(NH)_2$ ring in the crystal, but the position of the nitrogen atoms could not be determined precisely, since the nitrogen atoms are statistically distributed in the crystal structure. The unit cell dimensions are: a = 10.90 Å, b = 10.75 Å and c = 10.70 Å, β = 95.45°. The crystal density is 1.98 g/ccm and the melting point is F = 104–105°C.

The infrared spectrum shows that the associated imine is the 1,3-isomer of $S_6(NH)_2$. This association disappears, however, when the crystal is dissolved in a solvent. The molecular weight averaged from four cryoscopic measurements in benzene is indeed M = 183 (disassociation). In view of these results we were led to synthesize other molecular associations between S_8 and sulfurimines. We obtain in this way beautiful crystals of the following associations:

$2\ S_8 \rightarrow S_7(NH)$	$3\ S_8 \rightarrow S_6(NH)_2$ 1,3
$2\ S_8 \rightarrow S_6(NH)_2$ 1,3	$3\ S_8 \rightarrow S_6(NH)_2$ 1,4
$2\ S_8 \rightarrow S_4(NH)_4$ 1,3,5,7	$3\ S_8 \rightarrow S_5(NH)_3$ 1,3,5
	$3\ S_8 \rightarrow S_4(NH)_4$ 1,3,5,7

All these molecular associations have a well-defined formula and, as with other chemical species, the relations between S_8 and the sulfurimines are stoichiometric. The crystal unit cell of associations of 3 S_8 rings with 1 sulfurimine ring has the same space gr. P2/n and the same dimensions as the unit cell of γ-S_8. Similarly, the crystal unit cell of associations of formula $2\ S_8 \rightarrow 1$ sulfurimine ring has the same space gr. $P2_1/c$ and the same dimensions as that of monoclinic β-S_8. We therefore

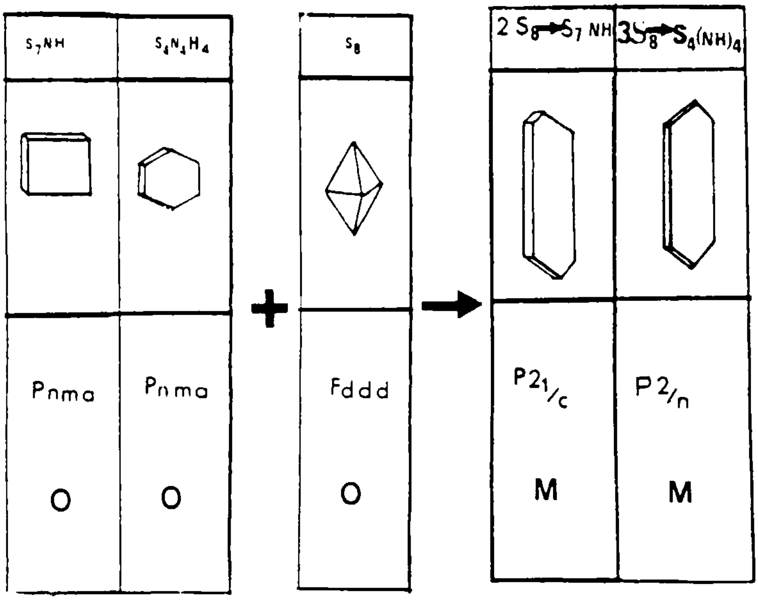
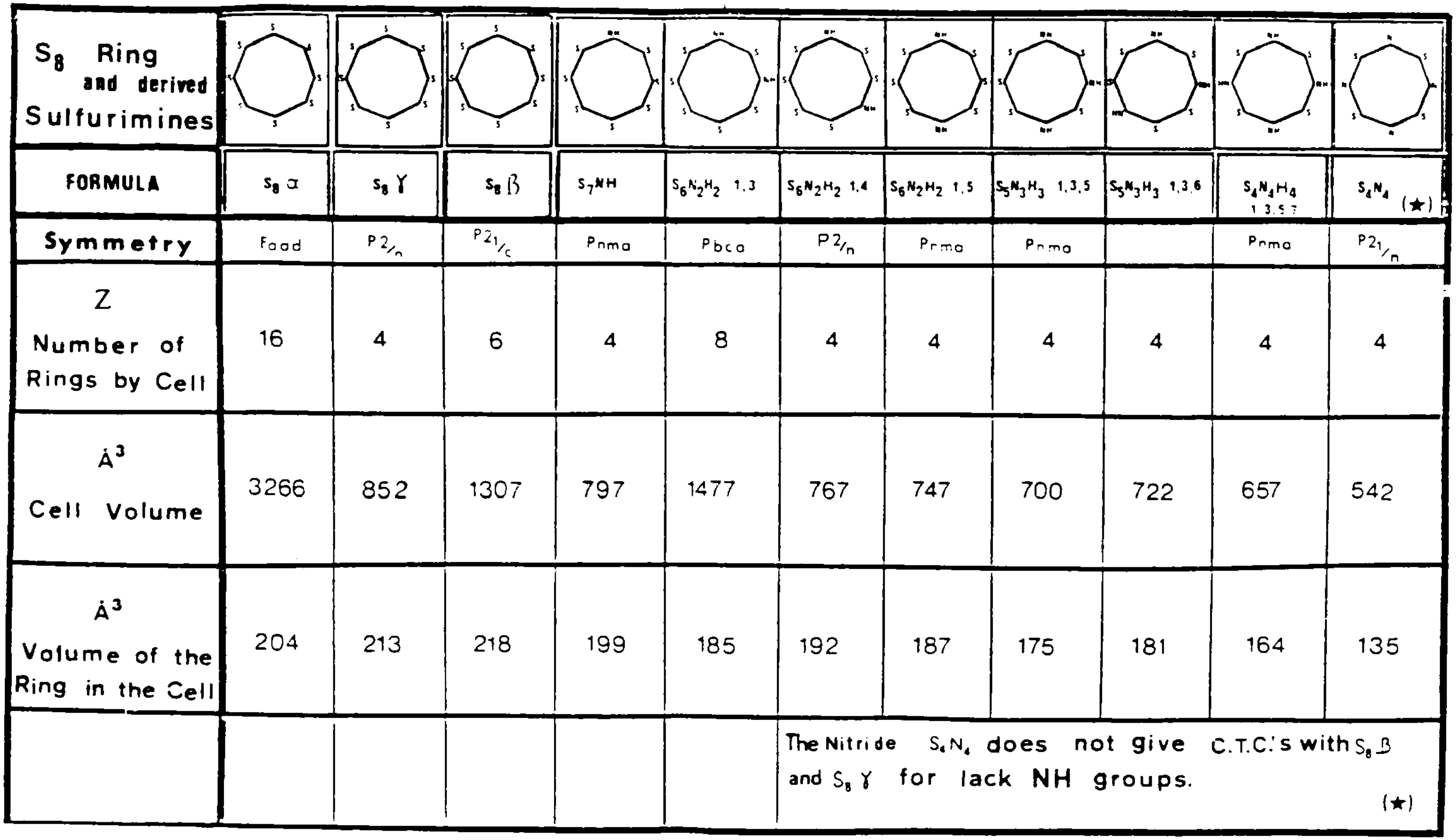


FIGURE 2

assume that they are formed by replacement in the unit cell of β-S_8 or γ-S_8 of a S_8 ring by a corresponding imine ring. The hydrogen bonds possibly have an influence on the stability of the new crystal structure, since the two unit cells of the monoclinic β- and γ-sulfurs are metastable at room temperature. In particular, the unit cell of β-S_8 is stable only above 95.5°C.

According to J. Zemann[4] the volume of the structural components is most determining for the occurrence of a given type of structure. One can deduce the volume of each sulfurimine molecule in the crystal from the volume of the unit cell and from the number Z of molecules it contains. A similar calculation permits us to determine the volume of the S_8 rings in the respective crystal structures of α-, β- and γ-sulfur (Figure 3). We can see that the volume of the sulfurimines ranges from



S_8 Ring and derived Sulfurimines											
FORMULA	$S_8\ \alpha$	$S_8\ \gamma$	$S_8\ \beta$	S_7NH	$S_6N_2H_2$ 1,3	$S_6N_2H_2$ 1,4	$S_6N_2H_2$ 1,5	$S_5N_3H_3$ 1,3,5	$S_5N_3H_3$ 1,3,6	$S_4N_4H_4$ 1,3,5,7	S_4N_4 (★)
Symmetry	Fodd	$P2/n$	$P2_1/c$	Pnma	Pbca	$P2/n$	Pnma	Pnma		Pnma	$P2_1/n$
Z Number of Rings by Cell	16	4	6	4	8	4	4	4	4	4	4
$Å^3$ Cell Volume	3266	852	1307	797	1477	767	747	700	722	657	542
$Å^3$ Volume of the Ring in the Cell	204	213	218	199	185	192	187	175	181	164	135
						The Nitride S_4N_4 does not give C.T.C.'s with $S_8\ \beta$ and $S_8\ \gamma$ for lack NH groups. (★)					

FIGURE 3

199 Å for S_7NH to 164 Å for $S_4(NH)_4$ and that it is smaller than the corresponding ones of β- and γ-S_8. It is therefore easily predictable that the position in the unit cell which is occupied by one of the β- or γ-S_8 ring (213 and 218 Å, resp.) can be easily exchanged for a sulfurimine ring. As for orthorhombic α-S_8 sulfur, this exchange never occurs, probably because of its small dimensions (204 Å) and its resulting greater lattice compactness α.

One can compare in Figure 4 the unit cell parameters of the two monoclinic forms of β- and γ-sulfur with the corresponding associations of the C.T.C's or associations $S_8 \rightarrow$ sulfurimines. This figure confirms the assumption that these associations really result from the substitution of a sulfurimine ring for a corresponding S_8 ring in the unit cell of β- and γ-sulfur. Their unit cells have the same symmetry and dimensions as those of β- and γ-sulfur. The remarkable stability of the resulting association is probably due to the presence of the imine NH groups and to the charge transfer NH ← S_8 ring. This transfer is manifest in the 3 $S_8 \rightarrow S_4(NH)_4$ complex, since the two components are insoluble in solvents such as CCl_4 when taken individually, while their complex is highly soluble. According to Mulliken's observations and to Andrews and Keefer's work (5), this is one of the characteristics of the C.T.C's. Moreover, the monoclinic crystal structures β-S_8 and γ-S_8 are not stable at room temperature, as already mentioned, and are transformed more or less rapidly into the orthorhombic form α-S_8. β-S_8, in particular, is stable only above 95.5 °C up to

γ S_8	γ S_8	$3S_8 \cdots S_4(NH)_4$	$3S_8 \cdots S_4(NH)_4$	$3S_8 \cdots S_5(NH)_3$ [1,3,5]	$3S_8 \cdots S_6(NH)_2$ [1,3]
a = 8,57 Å b = 13,05 ·· c = 8,23 ·· β = 112° 54′ V_0 = 852 Å³ $P2/_n$ ★ 1.	a = 8,442 Å b = 13,025 ·· c = 8,207 ·· β = 112° 38′ V_0 = 835 Å³ $P2/_n$ ★ 2.	a = 8,441 Å b = 13,034 ·· c = 8,203 ·· β = 112°30′ V_0 = 834 Å³ $P2/_n$ ★ 3.	a = 8,424 Å b = 13,023 ·· c = 8,227 ·· β = 112° 30′ V_0 = 834 Å³ $P2/_n$ ★ 4.	a = 8,424 Å b = 13,128 ·· c = 8,191 ·· β = 112° 30′ V_0 = 837 Å³ $P2/_n$ ★ 5.	a = 8,469 Å b = 13,023 ·· c = 8,227 ·· β = 113° 10′ V_0 = 830 Å³ $P2/_n$ ★ 6.

β S_8	β S_8	$2S_8 \cdots S_6(NH)_2$ [1,3]	$2S_8 \cdots S_6(NH)_2$ [1,3]	$2S_8 \cdots S_7NH$	$2S_8 \cdots S_7NH$
a = 11,02 Å b = 10,96 ·· c = 10,90 ·· β = 96,7° V_0 = 1307 Å³ $P2_1/_c$ ★ 7.	a = 10,890 Å b = 10,756 ·· c = 10,710 ·· β = 95,7° V_0 = 1248 Å³ $P2_1/_c$ ★ 8.	a = 10,883 Å b = 10,730 ·· c = 10,674 ·· β = 95,67° V_0 = 1241 Å³ $P2_1/_c$ ★ 9.	a = 10,900 Å b = 10,750 ·· c = 10,700 ·· β = 95,7° V_0 = 1247 Å³ $P2_1/_c$ ★ 10.	a = 10,960 Å b = 10,850 ·· c = 10,840 ·· β = 96° V_0 = 1275 Å³ $P2_1/_c$ ★ 11.	a = 10,907 Å b = 10,791 ·· c = 10,752 ·· β = 95,7° V_0 = 1260 Å³ $P2_1/_c$ ★ 12.

★ 1. Y. M. de Haan (6)
2. Y. Watanabe (7)
3. Mme Gasperin (8)
4. M. Herson
5. M. Herson
★ 6. M. Herson
7. D. E. Sands (measured 103° C)
8. " (9) (calculated 15° C)
9. Mme Gasperin
10. Mlle de Satgey (3)
★ 11. Mme Gasperin (10)
12. M. Herson

FIGURE 4

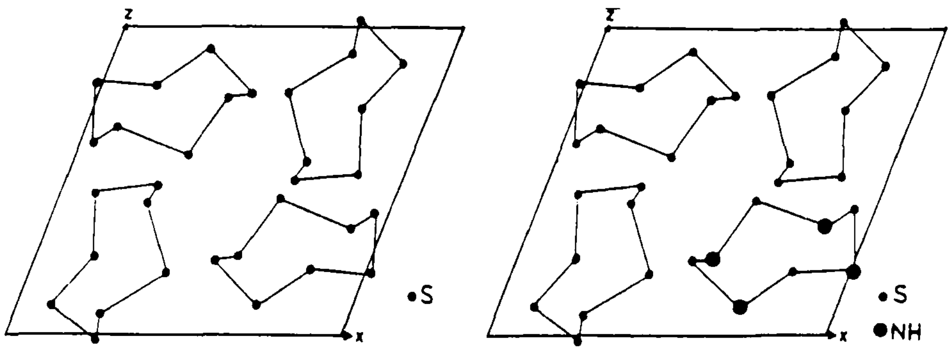
the melting point of this form at about 120°C:

$$\alpha S_8 \xrightarrow{95.5^\circ C} \beta S_8$$

On the other hand, $S_8 \rightarrow$ sulfurimines complexes are particularly stable at room temperature, as already indicated. The charge-transfer bonds are probably responsible for the stability of the new crystal structure. The C.T.C. bond energies are stronger than those of the hydrogen bonds and lie between the latter and the ionic bond energies:

Type of bond	energy	class of crystal	example
van der Waals	2 K cal/mol	molecular	sulfur
hydrogen	5 to 8 K cal/mol	molecular	ice
C.T.C.	10 to 31 K cal/mol	molecular	$I_2 \leftarrow S_8$
ionic	50 to 70 K cal/mol	ionic	NaCl
covalent	150 K cal/mol	atomic	diamond

The analogy between the unit cell of the $3\ S_8 \rightarrow S_4(NH)_4$ complex and that of monoclinic γ-sulfur clearly appears in Figure 5. In the complex the imine $S_4(NH)_4$ ring has a statistical position and lies, depending on the unit cells, in 4 possible positions, nitrogen and sulfur occupying in this ring interchangeable positions, which makes a total of eight different possible positions. Figure 5 represents one of these 8 possible positions in the complex crystal structure. Similarly, the analogy between the unit cell of the charge transfer complex $[2\ S_8 \rightarrow S_6(NH)_2]_2$ and that of β-S_8 is clearly shown in Figure 6. The $S_6(NH)_2$ rings have several statistically possible positions in the unit cell. Figure 6 shows one of the 12 possible positions of the two $S_6(NH)_2$ rings in the crystal cell.



γS_8 $3S_8 \cdot\rightarrow S_4(NH)_4$

FIGURE 5

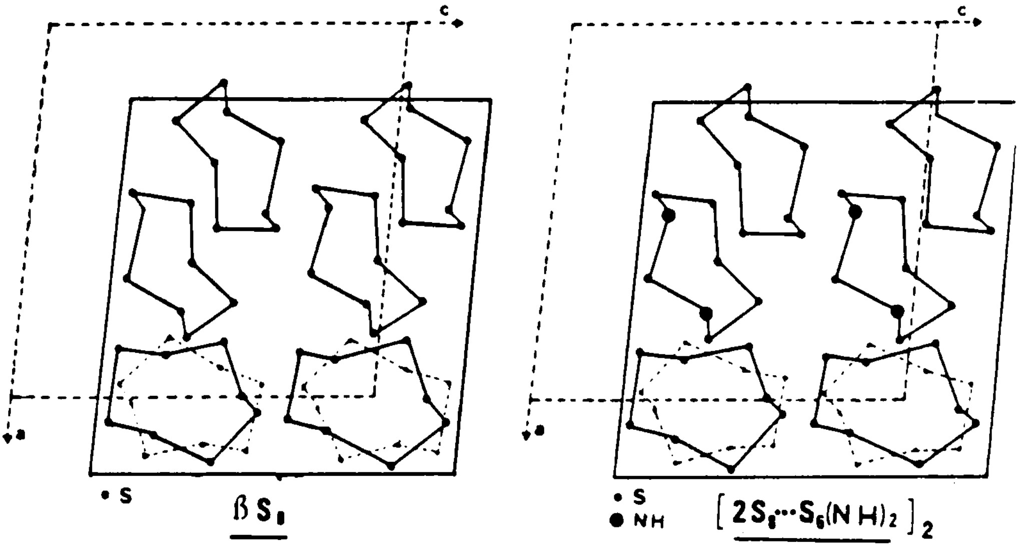


FIGURE 6

Structure determination of 3 $S_8 \rightarrow S_4(NH)_4$

We have studied by X-ray technique a single crystal obtained as a transparent yellow prisma elongated along the *c*-direction and flattened perpendicularly to *b*, with dimensions 0.40 × 2 × 0.1 mm. The X-ray study was based on data collected on a Philips diffractometer, type PW 1100, fitted with a graphite monochromator. 2529 reflections were measured up to $\theta = 30°$ using MoKα radiation. The procedure used was a classical one and was based on the three-dimensional Patterson cross-sections. Refinements were made by the least-squares method up to a factor R = 0.039 for 1557 non-zero reflections such that $F_{min} \geqslant F_{max}/25$. The best fit was obtained by considering a unique atom A such that A = (7 S + N)/8.

The structure is identical with that of monoclinic γ-sulfur described by Watanabe.[7] It contains four rings of 8 A atoms corresponding each to each by the center of symmetry (Figure 5). The measured crystal cell parameters are: $a = 8.440$, $b = 13.034$, $c = 8.203$ Å, $\beta = 112.49°$, space group P2/*n*, A—A distances = 2.041 (0.02) Å, A—A—A = 107.84 (0.05)°.

In conclusion, the statistical configuration obtained by this structure determination shows that the $S_4(NH)_4$ ring (the existence of which is confirmed by the infrared absorption spectra) lies, depending on the unit cells, in 4 possible positions and that nitrogen and sulfur occupy in this ring alternating or interchangeable positions.

Structure determination of 2 $S_8 \rightarrow S_6(NH)_2$

X-ray investigation was also carried out on the basis of the three-dimensional Patterson cross-sections. Refinements were made by the least-squares method up to a factor R = 0.066 for 2568 reflections.

Here again, the best fit was obtained when considering a unique A atom such that A = (11 S + N)/12, which proves that in all sites nitrogen and sulfur occupy an alternating position depending on the unit cells. The structure is identical with that of β-sulfur described by Sands.[9] It contains 4 rings with 8 elements placed in general positions and two rings placed in special positions which are likely to occupy two possible positions related by a center of symmetry (Figure 6). The dimensions found are: a = 10.883, b = 10.730, c = 10.674 Å, β = 95.67°; space gr. $P2_1/c$. In the two complexes studied the intermolecular distances are generally van der Waals distances (about 3.70 Å, as indicated by Pauling), but one also finds shorter distances ranging from 3.43 and 3.62 Å For $3\ S_8 \rightarrow S_4(NH)_4$ and from 3.37 and 3.50 Å for the $2\ S_8 \rightarrow S_6(NH)_2$ complex. Lastly, in each molecule the ring with 8 atoms consists of two squares of 4 atoms each, distant by 0.99 Å and making an angle of 45° with respect to each other.

All $S_8 \rightarrow$ sulfurimine complexes studied here make exceptions to the Mitscherlich rule which states that "crystals with the same structural unit and the same dimensions have the same chemical composition". It is indeed obvious from the preceding two examples that two identical unit cells, such as γ-S_8 and $3\ S_8 \rightarrow S_4(NH)_4$ have not the same chemical composition. Mitscherlich's rule has been extended by Goldschmidt to compounds with the same structure that he referred to as isotypes.

Similarly, the crystallochemical analysis of Federov, which consists of determining the chemical formula of a compound by measuring the angles of its crystals on a goniometer, cannot be applied here, since two crystals with the same measured angles can correspond to different chemical species.

Infrared and ultraviolet spectrography of the C.T.C's: n $S_8 \rightarrow S_{8-n}(NH)_n$

The chemical and crystallographical data on the C.T.C's of $S_8 \rightarrow$ sulfurimines reported above do not give sufficient information on the NH groups of the sulfurimines and on the hydrogen bonds. We have studied the infrared spectra (11) of the $2\ S_8 \rightarrow S_7NH$ and $3\ S_8 \rightarrow S_4(NH)_4$ complexes in the range 3600–400 cm^{-1}, in the

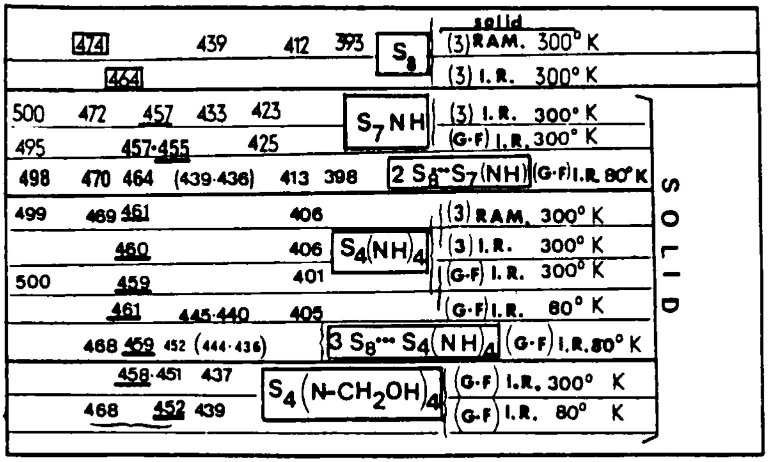


FIGURE 7

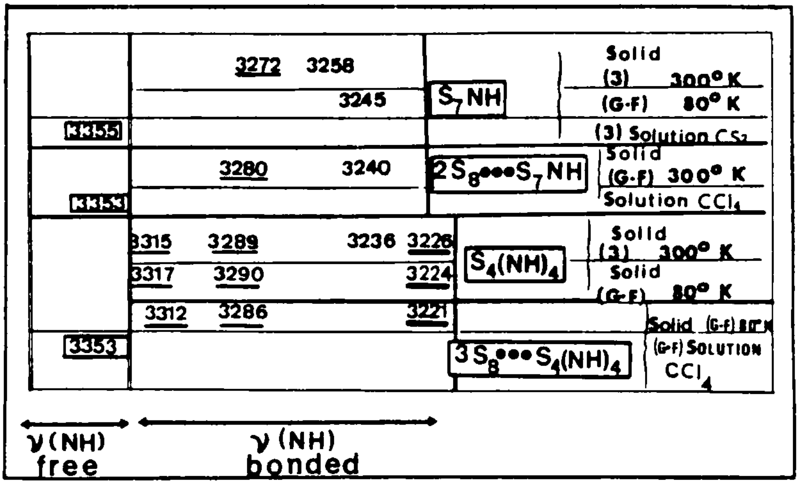


FIGURE 8

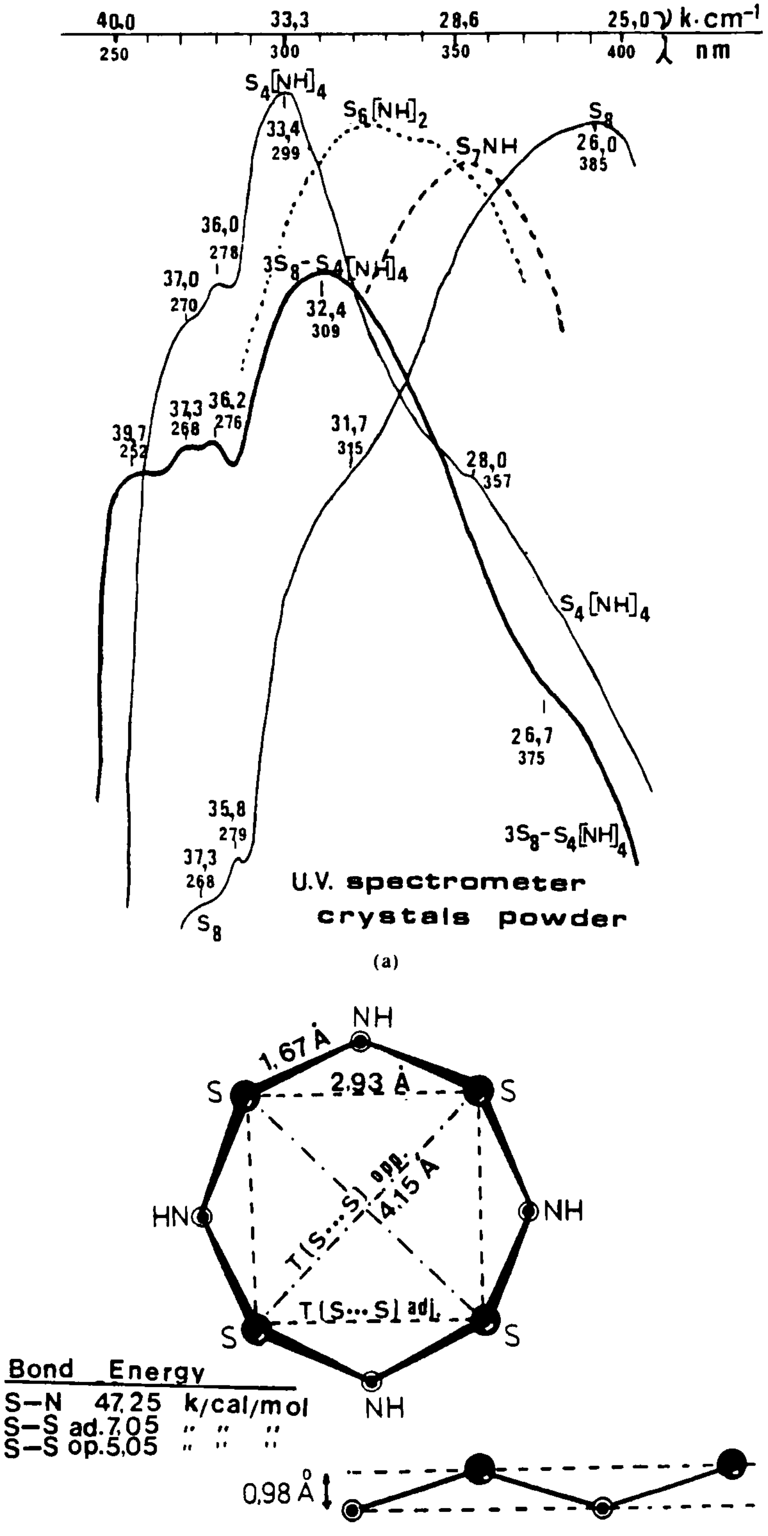
solid state and in a solution highly diluted in CCl_4 and we have compared these spectra with those of the pure imines S_7NH and $S_4(NH)_4$. We have used in this study the results obtained by C. Domingo and J. Orza[12] on S_8. The results are reported in Figures 7–8.

The presence of the NH group is characterized by the following valence vibrations: a) γ(NH) free at 3353 cm^{-1} for solutions in CCl_4 and b) ν(NH) bonded between 3320 and 3220 cm^{-1} with several components attributable for the solids to intermolecular NH ← S, NH ← N or NH ← ring bonds, the latter being of a type well-defined for I_2 ← benzene bonds.

In our analysis of the infrared spectra in the range 900–400 cm^{-1} (Figure 8), we were faced with the problem, already mentioned by other authors, of assigning the electronic structure of cyclic sulfurimines and, in particular, of $S_4(NH)_4$. Most authors[12] assign them to ν(S—N), ν(S—S) and ν(S—S—S), but the vibration 460 cm^{-1} poses a problem: it is generally considered as characteristic of the S—S bond which does not exist in $S_4(NH)_4$, but is found in this compound. It is assigned to (NH) (or out-of-plane NH vibration).

Now, we have observed this vibration for $S_4(NH)_4$, 3 $S_8 \rightharpoonup S_4(NH)_4$ and, more particularly, for $S_4(CH_2OH)_4$, although the NH group does not exist in the latter compound. It seems, therefore, that in the electronic structure, which is presently accepted for $S_4(NH)_4$ and similar compounds, we must take account of the multiple sulfur valencies and admit transannular bonds, also called Dewar cross-conjugations, which are similar to those of the P_4N_4 ring, the existence of which has been established by various techniques, in particular by magnetic rotating polarization (Faraday effect).

The ultraviolet spectrographic investigation by diffuse reflection on crystals confirms the existence of charge-transfer complexes of sulfur-sulfurimine. Ultraviolet techniques were indeed always used to establish the existence of such $D^+ \rightharpoonup A^-$ complexes (ex: $C_6H_6 \rightharpoonup I_2$ in solution). We have recorded the spectra at 300°C between 400 and 200 nm (25 to 50 K cm^{-1}) with a Cary model 16 spectrophotome-


40,0
33,3
28,6
25,0 ν k·cm⁻¹
250
300
350
400 λ nm
S4[NH]4
33,4
299
S6[NH]2
S7NH
S8
26,0
385
36,0
278
37,0
270
3S8-S4[NH]4
32,4
309
39,7
252
37,3
268
36,2
276
31,7
315
28,0
357
S4[NH]4
26,7
375
3S8-S4[NH]4
35,8
279
37,3
268
S8
U.V. spectrometer
crystals powder
1,67 Å
2,93 Å
T(S···S) opp. 4,15 Å
T(S···S) adj.
NH
S
S
HN
NH
S
S
NH
Bond Energy
S–N 47,25 k/cal/mol
S–S ad. 7,05 " " "
S–S op. 5,05 " " "
0,98 Å

(a)

(b)

FIGURE 9

ter by the method of diffuse reflection on the crystal powder, compared to calcium (or MgO) carbonate as the reference. This well-known technique, which is not much used, however, does not give correct measurements of the position (5 to 10 nm) and contour of the wide bands (as is the case here), but permits us to avoid interactions between the solvent and the thioimine NH which would destroy the complex being analyzed.

As can be seen in Figure 9, the spectrum characteristic of the $3\ S_8 \rightarrow S_4(NH)_4$ complex is distinct from that of the thioimine $S_4(NH)_4$:

1) For S_8 the wide band is intense at 26.0 K cm^{-1} (385 nm) and accompanied by a band at 31.7 K cm^{-1} (315 nm); for $S_4(NH)_4$ the band at 28.0 K cm^{-1} is only an inflection, while that at 33.4 K cm^{-1} is intense. On the other hand, for $3\ S_8 \rightarrow S_4(NH)_4$ the band at 26.7 K cm^{-1} (close to, but distinct from that of sulfur at 26.0 K cm^{-1}) is weak, while that at 32.4 K cm^{-1} is wide and intense.

2) For $S_4(NH)_4$, $S_6(NH)_2$, $S_7(NH)$ and S_8, the intense wide band is observed between 33.4 and 26.0 K cm^{-1} (see section II). On the other hand, for the $3\ S_8 \rightarrow S_4(NH)_4$, $2\ S_8 \rightarrow S_6(NH)_2$ and $2\ S_8 \rightarrow S_7NH$ complexes the characteristic band remains close to 32.4 K cm^{-1} (only the first case is shown in the figure).

3) In all spectra studied—of sulfur, thioimines and their complexes—we find two bands (weak/sharp) at about 37.3 and 36.2 K cm^{-1}. They therefore correspond to sulfur (and not to nitrogen).

To sum up, we can therefore confirm the existence of the following charge-transfer complexes (C.T.C.):

Isotypes of β-sulfur: $2\ S_8 \rightarrow S_7NH$, $2\ S_8 \rightarrow S_6(NH)_2$,

Isotype of γ-sulfur: $3\ S_8 \rightarrow S_4(NH)_4$.

II. ORIGIN OF THE ELECTRONIC TRANSITIONS OF S_8, $S_n(NH)_{8-n}$ AND S_4N_4

After having established the existence of the complexes, we have been led to study the origin of the electronic transitions observed for the corresponding components (Figure 10). Despite the importance of sulfur, very few authors have studied these transitions: M. Fukuda in 1922,[25] H. Garcia-Fernandez in 1959,[26] D. Chapman and T. C. Waddington,[27] P. S. Bratermann,[28] J. B. Mason,[29] R. E. Davies.[30] We have reported in Figure 10, the experimental data available so far together with the values of Figure 9a.

For these various compounds the assignments of the electronic transitions have been made more particularly for the five ultraviolet bands of S_4N_4 and the results obtained by the various authors diverge:

For the most intense band at about 38.9 K cm^{-1} D. Chapman and T. C. Waddington[27] suggest a $\pi \rightarrow \pi^*$ transition, whereas P. S. Braterman[28] proposes a $\sigma \rightarrow \sigma^*$ transition and J. B. Mason[29] predicts a $n \rightarrow \pi^*$ transition (on the basis of the nuclear resonance of ^{14}N).

The assignments made by Braterman were based on the fact that he observed no band above 43.5 K cm^{-1} for $S_4(NH)_4$, a result which disagrees with ours for both the powder and the solution in CH_3OH.[31]

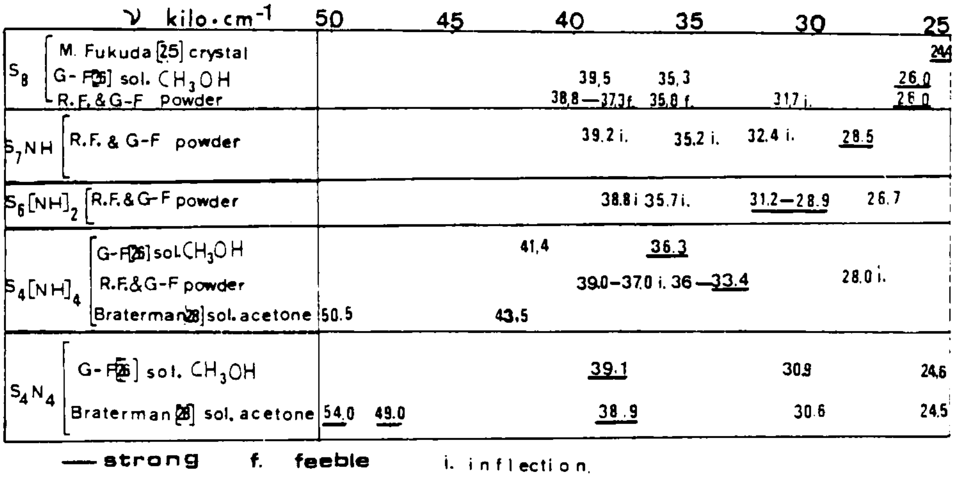


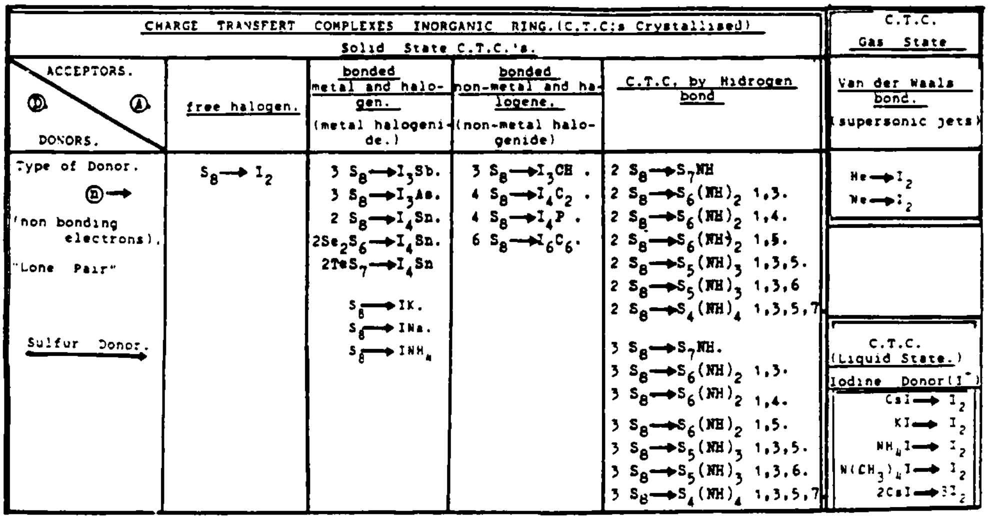
FIGURE 10

As already mentioned by J. B. Mason, our experiments (which ought to be repeated at 4°C) confirm the necessity of checking the assignments of the electronic transitions made for S_4N_4, $S_4(NH)_4$, and, more particularly, for S_8, for which, as far as we know, a theoretical study is paradoxically lacking.[30]

The charge transfer complex of sulfur-iodine, n $S_8 \rightarrow I_2$

The existence of the C.T.C. *n* $S_8 \rightarrow I_2$ (analogous to the well-known $C_6H_6 \rightarrow I_2$ complex) has been discussed long since: by Auger in 1908,[32] Demassieux in 1909[33] and, more particularly, Feher in 1961.[34] Jander and Turk[35] have shown in 1963, by measuring the solubility of a mixture of sulfur and iodine in dichloromethane, the existence in solution of a C.T.C. *n* $S_8 \rightarrow I_2$ of probable formula: 4 $S_8 \rightarrow I_2$, that they could not isolate in the crystalline solid state.

We have succeeded in obtaining crystals of the *n* $S_8 \rightarrow I_2$ complex by the following procedure: 3 g of crystallized sulfur and 1 g of iodine were dissolved in 50 ccm of benzene heated at 70°C in a small flask fitted with a ground-glass stopper secured with a metallic spring to prevent a loss of solvent by evaporation. The mixture was heated for 2 hours, allowed to cool, then the excess sulfur was allowed to settle and to crystallize. Besides the formation of octahedral sulfur crystals and iodine needles with a metallic glitter, one observed a few crystals which were characteristic of the sulfur-iodine C.T.C. They were hexagonal and very elongated in shape, amber-coloured (Figure 12) and their analysis revealed the composition *n* $S_8 \rightarrow I_2$ (probably 2 $S_8 \rightarrow I_2$). (Iodine was determined with a 0.1 N solution of Na thiosulfate in the presence of starch. We have recorded the electronic absorption spectra (ultraviolet and visible region at 300K) of S_8, *n* S_8—I_2 and I_2 in the solid state. Let us remember that the method used here, which consisted of comparing the diffusion of the polycrystal studied with that of magnesia, presents some drawbacks which are due to the fact that the band relative intensities could be determined only within a few K cm^{-1} and were therefore difficult to compare.



	CHARGE TRANSFERT COMPLEXES INORGANIC RING.(C.T.C:s Crystallised) Solid State C.T.C.'s.				C.T.C. Gas State
ACCEPTORS. Ⓓ Ⓐ DONORS.	free halogen.	bonded metal and halogen. (metal halogenide.)	bonded non-metal and halogene. (non-metal halogenide)	C.T.C. by Hidrogen bond	Van der Waals bond. (supersonic jets)
Type of Donor. ⓝ→ (non bonding electrons). "Lone Pair" Sulfur Donor.	$S_8 \rightarrow I_2$	$3\ S_8 \rightarrow I_3Sb.$ $3\ S_8 \rightarrow I_3As.$ $2\ S_8 \rightarrow I_4Sn.$ $2Se_2S_6 \rightarrow I_4Sn.$ $2TeS_7 \rightarrow I_4Sn$ $S_8 \rightarrow IK.$ $S_8 \rightarrow INa.$ $S_8 \rightarrow INH_4$	$3\ S_8 \rightarrow I_3CH.$ $4\ S_8 \rightarrow I_4C_2.$ $4\ S_8 \rightarrow I_4P.$ $6\ S_8 \rightarrow I_6C_6.$	$2\ S_8 \rightarrow S_7NH$ $2\ S_8 \rightarrow S_6(NH)_2$ 1,3. $2\ S_8 \rightarrow S_6(NH)_2$ 1,4. $2\ S_8 \rightarrow S_6(NH)_2$ 1,5. $2\ S_8 \rightarrow S_5(NH)_3$ 1,3,5. $2\ S_8 \rightarrow S_5(NH)_3$ 1,3,6 $2\ S_8 \rightarrow S_4(NH)_4$ 1,3,5,7 $3\ S_8 \rightarrow S_7NH.$ $3\ S_8 \rightarrow S_6(NH)_2$ 1,3. $3\ S_8 \rightarrow S_6(NH)_2$ 1,4. $3\ S_8 \rightarrow S_6(NH)_2$ 1,5. $3\ S_8 \rightarrow S_5(NH)_3$ 1,3,5. $3\ S_8 \rightarrow S_5(NH)_3$ 1,3,6. $3\ S_8 \rightarrow S_4(NH)_4$ 1,3,5,7	$He \rightarrow I_2$ $Ne \rightarrow I_2$ C.T.C. (Liquid State.) Iodine Donor(I^-) $CsI \rightarrow I_2$ $KI \rightarrow I_2$ $NH_4I \rightarrow I_2$ $N(CH_3)_4I \rightarrow I_2$ $2CsI \rightarrow 3I_2$

FIGURE 11

As can be seen in Figure 12, the existence of the sulfur-iodine C.T.C. is demonstrated by three points: 1) the transitions of I_2 (16.8 and 17.9 K cm^{-1}) are most intense, where *n* $S_8 \rightarrow I_2$ only exhibits a weak inflection in this range. In S_8 this band is absent, which seems to be a most convincing argument. 2) The *n* $S_8 \rightarrow I_2$ complex gives only a very weak band at about 19 K cm^{-1} which does not appear for I_2. 3) The range 25 K cm^{-1} is less characteristic. I_2 shows a weak band at about 23.3 K cm^{-1}, but for *n* $S_8 \rightarrow I_2$ and S_8 (24.7 and 25.6, resp.) the difference is about within the experimental error.

Charge-transfer complexes were reported for the first time in 1948 by Benesi and Hildebrand.[16] When studying the ultraviolet absorption spectrum of an iodine solution in benzene, they observed a very marked band at about 2970 Å which was absent in the spectra of the pure components. This band proves the existence of a new compound that Mulliken and other authors have termed charge-transfer complex, since it corresponds to a molecular association resulting from the transfer of an electron from one molecule (Donor) to another (Acceptor). The mechanism of formation of the C.T.C's is therefore a partial charge transfer from one compound, which tends to donate electrons (Lewis bases), to another which tends to accept them (Lewis acids). The bond is energetically a little stronger than the hydrogen bond and varies between 8 and 30 K cal/mol. According to Mulliken's theory, the complex stability is due to a resonance between the form D + A, a mixture of donor + acceptor chemically non-bonded, and an ionic structure after complete transfer D^+A^- of an electron:

$$[D + A] \rightarrow [D^+\ \ A^-]$$

Aromatic, polyaromatic, ethylenic, acetylenic, carbides, amines, imines, nitriles, amine oxides, dioxan, ethers, etc. are donors. Boranes, F, Cl, Br, I, OH, NO_2, quinones, nitrobenzene, etc. are acceptors.

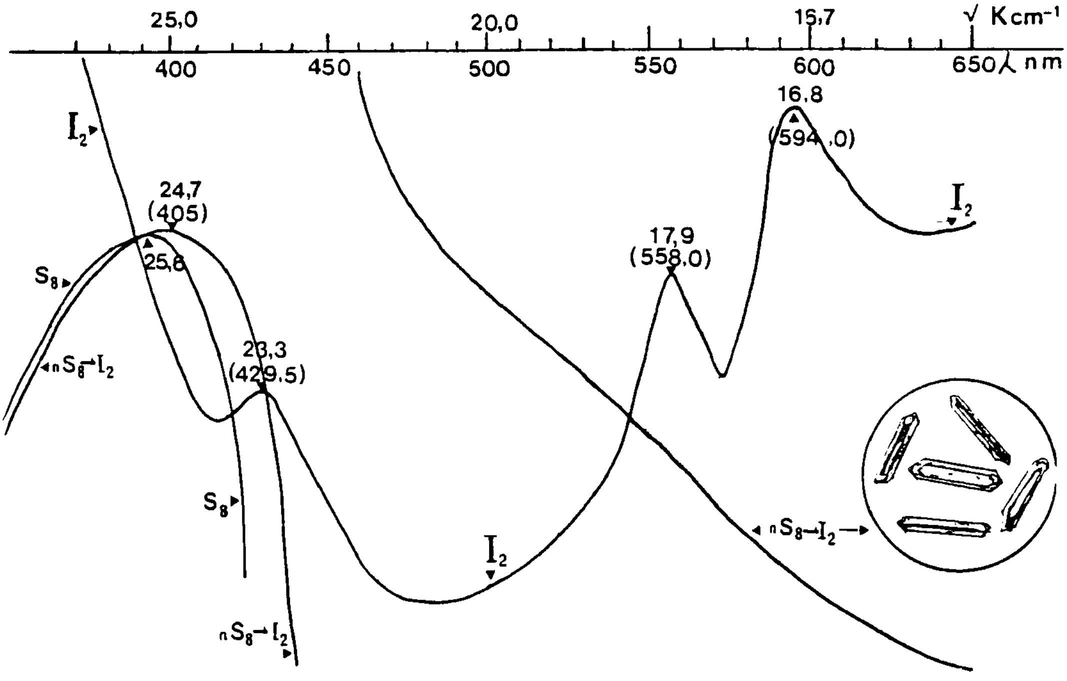


FIGURE 12

According to Fergusson[18] a transferred electron would vibrate from the donor to the acceptor with a transition moment of high intensity. It has been shown by NMR that in the $Br_2 \leftarrow C_6H_6$ complex, the transfer occurs through an electron of the ring to Br. On the other hand, in the $Br \rightarrow C_6H_6$ complex the charge transfer occurs through an electron of the free pair from Br to the benzene ring. This can be explained by the very close values of the ionization potentials of the ring electrons and of those of the free pair in Br.

According to Dewar the donor D has occupied orbitals of high energy, but the acceptor A has unoccupied orbitals of very low energy. A transition therefore consists in the transfer of an electron from the donor D to the acceptor A, as schematized in Figure 13.

In the absorption spectrum of the A and B components of a complex, the frequency of the ultraviolet or visible maximum absorption band of each component varies very little. The Cl · · · Benzene complex forms an exception: the absorption of Cl is a maximum here in the ultraviolet region, but the absorption band of Cl in the pure state lies in the visible region. The wave length of the C.T.C. maximum absorption band increases with ionization energy of the donor when using the same acceptor:

[Benzene] → [I—Cl] $\lambda = 2970$ Å
[Naphtalene] → [I—Cl] $\lambda = 3600$ Å
[Anthracene] → [I—Cl] $\lambda = 4300$ Å

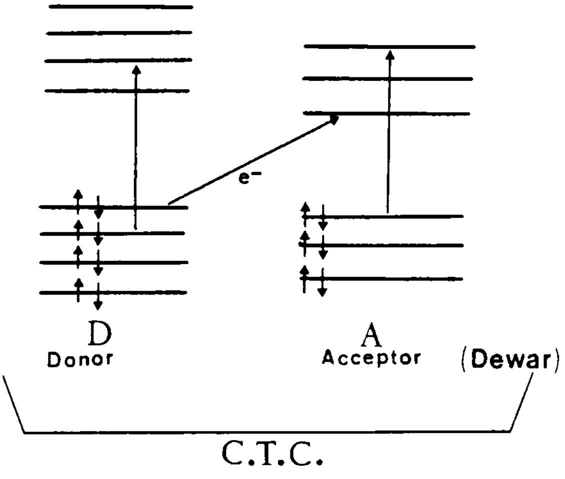


FIGURE 13

In the C.T.C. the difference of frequency between the band corresponding to the charge transfer and the maximum of the band of longest wave length of the donor ν_{CTC} is constant:

$$\Delta\nu = \nu_D - \nu_{CTC} = \text{Const.}$$

As a result, the C.T.C. absorption wave length is always longer than that of the donor. Concerning the acceptor, the importance of its band shift is a measure of the importance of the charge transfer and of the ionization rate of this acceptor. Iodine, for instance, has an absorption band at $\lambda = 5200$ Å. This band is more or less shifted towards the ultraviolet region up to 4000 Å. The latter band corresponds to the absorption band of the negative I^- ion.

The structure of a few C.T.C's in the solid state was determined by X-ray diffraction technique. The C.T.C. $C_6H_6 \rightarrow I_2$ has a structure which retains the symmetry of benzene, iodine lying on the axis of symmetry of C_6H_6 and along its direction (Figure 14c).

III. CRYSTAL STRUCTURE AND FACIES OF THE C.T.C.'S

C.T.C. crystals are in general very elongated along the direction of molecular stackings, which, according to Hartman and Perdok,[19] are Periodic Bonds Chains (P.B.C.), and the overlapping bonds favor crystal growth along this direction better than do lateral hydrogen bonds (Figure 14). In the C.T.C's the axis of stacking coincides in general with the direction of elongation. The charge-transfer bonds have a marked directional character, the nature of which has been described by Dewar and Mulliken.[20] The corollary of the charge transfer is a high electrical conductivity of the crystal.

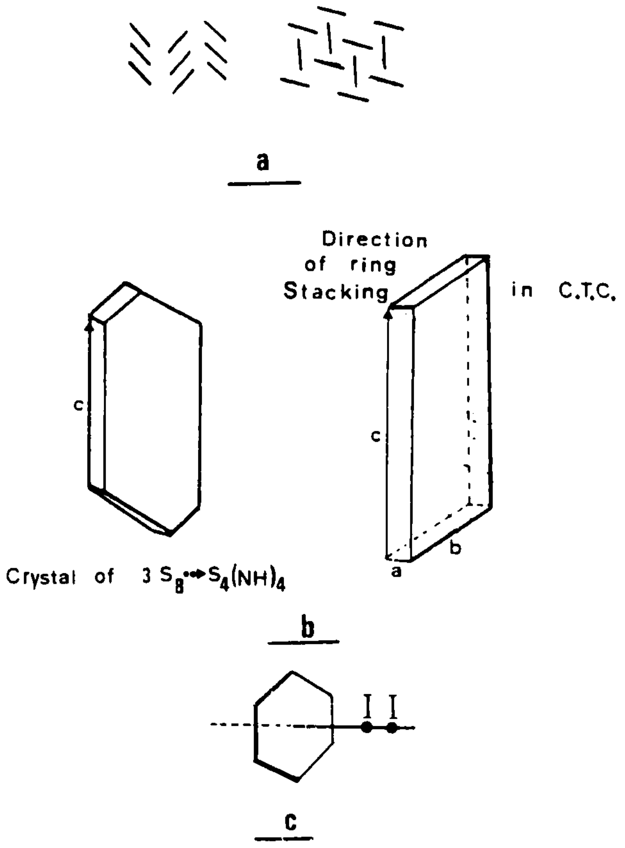


FIGURE 14

Overlapping bonds in crystals with cyclic molecules are often characterized by a stacking with parallel axes or by a ring compactness. The overlapping of molecules generally occurs as a result of a short translation of the lattice or of a center of symmetry between planes,[21] the distance between molecular planes being little inclined with respect to the axis of stacking. This is the case in large molecules with condensed rings, such as graphite, perylene, etc. On the other hand, isolated rings, such as S_8 and the sulfurimines, exhibit in most cases a herring-bone structure (Figure 14b) and stacking sometimes occurs via overlapping. According to Kitaodgoriskii,[22] the maximum compactness corresponds to an atom from one ring which overlaps another atom from the ring of the preceding layer, π-orbitals being involved in the directed bonds. This compactness never exists in practice (coefficient 1.00). Graphite has a very high coefficient (0.89) and the shift from one plane to the following is only 0.8 Å, which represents an angular deviation of 13° with respect to the normal of the C_6 rings, the distance between planes being 3.35 Å. The compactness is probably determined by the structure arrangement which represents the minimum energy potential and often results from the special electronic configuration of each molecule. The molecule stacking in the crystal therefore depends on two main factors:

1) a bonding due to the displacement of the π-electrons,

2) a bonding due to a polar group or bond (ex. NH groups).

The C.T.C's of $S_8 \rightarrow$ sulfurimines comprise a resonating S_8 ring juxtaposed to a heterocycle in which the position of the polar NH group is determining for the crystal structure configuration.

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