



The X-ray crystallographic determination of the structures of the CIS para-menthane thiourea adduct and 1,2,4 trichlorobenzene-1,2,4 trimethylbenzene thiourea adduct
by Mark John Spinti

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE
in Chemical Engineering
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Abstract:

Thiourea's unusual ability to form adducts with hydrocarbons shows promise as a method of separating hydrocarbon mixtures. In an attempt to better understand the forces which hold thiourea adducts together, the crystal structure of two thiourea adducts were determined by x-ray crystallography. A diffractometer data set was collected on a crystal of the thiourea adduct with cis para-menthane. This structure was solved in the space group $R\bar{3}m$ in a hexagonal unit cell with parameters of $a=b=15.935(2)$, $c=12.489(2)$, $\alpha=\beta=90.0^\circ$ and $\gamma=120.0^\circ$. The disorder of the cis para-menthane molecule was successfully modeled and refinement gave a R value of 0.0670.

Another diffractometer data set was collected on a crystal of the thiourea adduct containing a 50 mole percent mixture of 1,2,4 trimethylbenzene and 1,2,4 trichlorobenzene. This aromatic-thiourea adduct was solved in the space group $P2_1/c$ in a monoclinic unit cell with parameters of $a=9.886(7)$, $b=15.245(8)$, $c=12.313(6)$, $\alpha=\gamma=90.0^\circ$, and $\beta=112.48^\circ$ (4). The aromatic molecules in this adduct are disordered and no model was found for them.

Both of these adduct structures are consistent with the structure of other similar thiourea adducts. Evidence, in the form of interatomic distances, for an interaction between the sulfur atom of thiourea and OH groups of the cis para-menthane molecule was found. It was concluded that a dipole-dipole interaction exists between the sulfur atom of thiourea and C-H groups of the cis para-menthane molecule.

THE X-RAY CRYSTALLOGRAPHIC DETERMINATION OF THE STRUCTURES
OF THE CIS PARA-MENTHANE THIOUREA ADDUCT AND 1,2,4 TRI-
CHLOROBENZENE-1,2,4 TRIMETHYLBENZENE THIOUREA ADDUCT

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Mark John Spinti

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APPROVAL

of a thesis submitted by

Mark John Spinti

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

Thiourea's unusual ability to form adducts with hydrocarbons shows promise as a method of separating hydrocarbon mixtures. In an attempt to better understand the forces which hold thiourea adducts together, the crystal structure of two thiourea adducts were determined by x-ray crystallography.

A diffractometer data set was collected on a crystal of the thiourea adduct with cis para-menthane. This structure was solved in the space group $R\bar{3}bar$ in a hexagonal unit cell with parameters of $a=b=15.935(2)$, $c=12.489(2)$, $\alpha=\beta=90.0^\circ$ and $\gamma=120.0^\circ$. The disorder of the cis para-menthane molecule was successfully modeled and refinement gave a R value of 0.0670.

Another diffractometer data set was collected on a crystal of the thiourea adduct containing a 50 mole percent mixture of 1,2,4 trimethylbenzene and 1,2,4 trichlorobenzene. This aromatic-thiourea adduct was solved in the space group $P2_1/c$ in a monoclinic unit cell with parameters of $a=9.886(7)$, $b=15.245(8)$, $c=12.313(6)$, $\alpha=\gamma=90.0^\circ$, and $\beta=112.48^\circ(4)$. The aromatic molecules in this adduct are disordered and no model was found for them.

Both of these adduct structures are consistent with the structure of other similar thiourea adducts. Evidence, in the form of interatomic distances, for an interaction between the sulfur atom of thiourea and C-H groups of the cis para-menthane molecule was found. It was concluded that a dipole-dipole interaction exists between the sulfur atom of thiourea and C-H groups of the cis para-menthane molecule.

INTRODUCTION

Background

Pure compounds are often required in polymeric and synthetic processes. Requirements for pure compounds cause pure compounds to be of greater value than mixtures. If the separation and purification of the compound is difficult, the cost of the separation process can be prohibitive. The high costs of separating hard-to-separate systems leads to the demand for new separation techniques.

The separation of hydrocarbon mixtures is a common industrial process. Most separation processes take advantage of differences in physical properties: for example, distillation is based on differences in volatility. Quite often isomers of a given empirical formula have nearly the same physical properties, which makes the separation of isomers very difficult. Other hydrocarbon mixtures which contain compounds with similar physical properties also pose separation problems.

One novel separation technique is extractive crystallization. In extractive crystallization a given compound selectively forms an adduct with the desired compound. Isomers and some classes of hydrocarbons can be separated using extractive crystallization.

An adduct is a crystal which contains two or more compounds. When an adduct crystal is dissolved, the compounds are released unchanged. The structure of an adduct contains "host" molecules in a cage-like arrangement which traps the "guest" molecule.

Urea and thiourea will act as the "host" molecules in some adducts. These adducts will only form with suitable "guest" molecules. A suitable "guest" is one with the appropriate chemical properties and molecular shape. Urea will form adducts with straight chain paraffins. Thiourea will form adducts with: branched paraffins, cyclopentane and cyclohexane and their derivatives, certain chloro compounds such as carbon tetrachloride, some branched and cyclic aldehydes, alcohols, and ketones (1,2). It was thought that benzenoid compounds would not form stable thiourea adducts unless they contain side groups which are proper adducting structures (e.g. benzylcyclohexane, tert-butylbenzene, or other highly substituted structures such as 1,2,4,5 tetramethylbenzene)(1). Recent studies have shown that o-xylene, pseudocumene (1,2,4 trimethylbenzene), and all three isomers of trichlorobenzene will adduct (3).

The reason for the difference between the compounds that will adduct with urea and the compounds that will adduct with thiourea is the size of the channel which traps

the guest molecule. Since the sulfur in thiourea is larger than the oxygen in urea, thiourea has a larger channel to trap guest molecules. An interesting characteristic of thiourea is that it is selective for some geometric-isomers (5).

Some compounds which by themselves will not form adducts can be induced to form adducts if an additional compound is present (4). This additional compound is termed an inductor.

Normally difficult separations can be made easier if induced extractive crystallization is used. McCandless has reported that C_9 alkylbenzenes and aromatic isomers can be separated using induced extractive crystallization (6). Different inductors are selective for different compounds. The role of the inductor is not fully understood.

Related Research



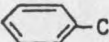


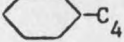
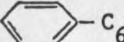
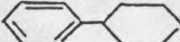


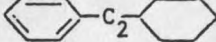

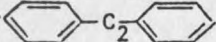
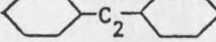
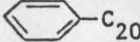

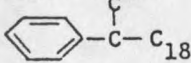
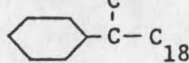
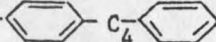
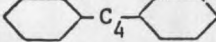


Urea adducts were accidentally discovered by M. F. Bengen in 1940 (1). He was using urea in a method of determining fat content in milk. Bengen added n-octyl alcohol to reduce frothing and observed the needle-like crystals characteristic of urea and thiourea adducts. Further study showed that higher alcohols, acids, n-paraffins and other straight-chained hydrocarbons form adducts with urea.

Thiourea adducts were discovered in 1947 by Fetterly (7) and independently in 1949 by Angla (2). Selenourea and tellurorea have also been found to form adducts with organic compounds (1). Thiourea will form adducts with some compounds that will not adduct with urea. The compounds which will adduct with thiourea include: branched-chained paraffins, naphthenic compounds, some ketones, carbon tetrachloride and a few other chloro-carbon compounds, and some compounds of the terpene, comphene and cyclohexane classes (1). Table 1 shows some compounds with the same number of carbon atoms, some of which will adduct with thiourea and some of which will not.

Pure thiourea has at least five different crystalline phases, depending on the temperature. The room temperature phase contains three groups of S--N interactions which

Table 1

Compounds which form adducts with thiourea compared
with compounds which do not form adducts
[reproduced from Mandelcorn (1)]

<u>Nonadducting</u>	<u>Adducting</u>	<u>Adducting</u>
Benzene 		Cyclohexane 
Toluene 		Methylcyclohexane 
n-Butylbenzene 		n-Butylcyclohexane 
n-Hexylbenzene 	Phenylcyclohexane 	n-Hexylcyclohexane 
n-Octylbenzene 	1-Phenyl-2-cyclohexylethane 	n-octylcyclohexane 
1,2-Diphenylethane 		1,2-Dicyclohexylethane 
1-Phenyleicosane 		2-Cyclohexyleicosane 
2-Phenyleicosane 		2-Cyclohexyleicosane 
1,4-Diphenylbutane 		1,4-Dicyclohexylbutane 
Tetraline 		Decalin 

involve hydrogen atoms (8). These distances are-- 3.394A, 3.526A, 3.696A.

X-ray crystallographic studies of urea adducts with n-hydrocarbons of lengths varying from C_8 to C_{50} were made by Smith (9) and Schlenk (4). These adducts crystallized in space group $C6_12-D_6^2$, with 18 urea molecules per unit cell and hexagonal lattice parameters $a=8.230$ A, $c=11.005$ A. The urea molecules form three interpenetrating spirals which are the walls of the hexagonal channels (1). The spirals are held together by hydrogen bonds between the nitrogen hydrogens and the oxygen atoms.

The hydrocarbon molecule is located in the channel formed by the honeycomb walls. The c-axis is parallel to the channel. The carbon chain length of the hydrocarbon molecules roughly corresponds to the c-axis length. X-ray crystallographic studies have determined the structures of some adducts. The urea molecule positions are well determined, but the hydrocarbon molecules are disordered. Analysis suggests the disorder of the hydrocarbon in the channel occurs because of rotation of the hydrocarbon molecule around its long axis. Three fixed, yet equivalent positions about 120° apart have been proposed by Fetterly (1).

In the urea network each oxygen atom is hydrogen bonded to four nitrogen atoms, and each nitrogen hydrogen is bonded to two oxygen atoms. These hydrogen bonds are of two types; one about 2.93 Å long and the other 3.04 Å long (10).

Thiourea adducts with non-aromatic hydrocarbons show a structure similar to that of urea adducts. The thiourea molecules form a rhombohedral unit cell, with a pseudo-hexagonal cell similar to that of urea adducts. The space group is $R\bar{3}m$, with hexagonal axis of $a=b=15.8$ Å, $c=12.5$ Å and eighteen thiourea molecules per unit cell (1). The c -axis roughly parallels the channel. As in urea adducts, the thiourea molecules form the honeycomb-shaped walls of the channel.

The unit cell and channel of thiourea adducts are larger than those of urea adducts because of the larger size of the sulfur atom in thiourea than the oxygen atom in urea. The channel diameter of urea is reported as 5.25 Å (1), that for thiourea is reported as 6.1 Å (2). The larger channel explains why thiourea forms adducts with different compounds than urea.

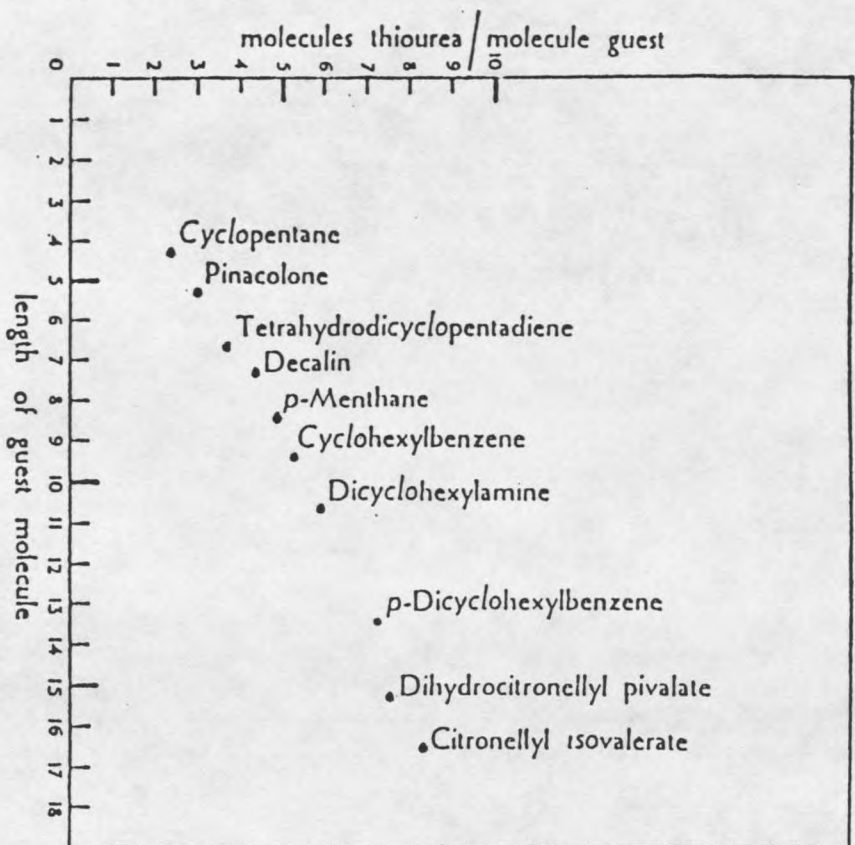
Schlenk found that as the guest molecule gets longer the mole ratio of urea molecules or thiourea molecules to organic increases (4). This increase causes the non-

stoichiometric relationship between the number of thiourea molecules and the number of guest molecules. Table 2 presents the length of the guest molecule plotted against the molar ratio of the number of thiourea molecules to the number of guest molecules. The ratio of thiourea molecules to guest molecules increases with increasing guest molecule length. This increase is caused by the guest molecule occupying a longer section of the channel as it, the guest molecule, gets longer in length.

Schlenk suggested an interaction between the urea molecule's oxygen atom and the guest hydrocarbon of about 2800 cal per CH_2 group (11). Fetterly discounted Schlenk's suggested interaction between the hydrocarbon CH_2 groups and the urea oxygen atom (1). In Fetterly's view no hydrogen bonding occurs between hydrocarbon groups and the urea oxygen atom. Fetterly claimed that the $\text{N-H}\cdots\text{O}$ hydrogen bonds in the urea structure is enough to hold the adducts together. This bond is shorter in the urea adduct (2.93 Å) than a similar bond in pure crystalline urea (2.99 Å). The shortening of this bond corresponds to a lower energy state. Fetterly proposes a new concept in hydrogen bonding, the "supported hydrogen bond". In his "supported hydrogen bond" a stronger hydrogen bond exists only if supported by an otherwise inert surface, (the channel hydrocarbon) which exerts only weak dispersion forces.

Table 2

Lengths of the guest molecule plotted against the molar ratio thiourea:guest [reproduced from Schlenk (4)]



The differences in the arrangement of the urea and thiourea molecules in their respective adducts can be seen in Figure 1. The arrows point from the oxygen or sulfur atom to the carbon atom of the urea or thiourea molecule. From the thiourea adduct structures Schlenk found that three sulfur atoms are coplanar (4). The sulfur atoms point straight into the center of the channel. These planes are 12.5Å apart in the c direction; this is the unit cell dimension along the c-axis. Figure 1 shows these planes as hatched areas.

The variation in the arrangement of the thiourea molecules in relationship to the channel causes a variation in the interaction forces between the thiourea molecules and the guest molecules. Schlenk predicted that the sites of maximum attraction correspond to the plane formed by the sulfur atoms (4). Regardless of where the sites of maximum interaction are located in the unit cell, the unit cell will only include one site of maximum interaction. Therefore, the thiourea molecules to guest molecules mole ratios of 3:1, 6:1, 9:1 or some other multiple of three, depending on the length of the guest molecule, will be favored. This is even true for some molecules which are not a multiple of $c/2$ in length. Schlenk claimed that hydrocarbon molecules fold or "slide together inside of the channel to give the multiples of three

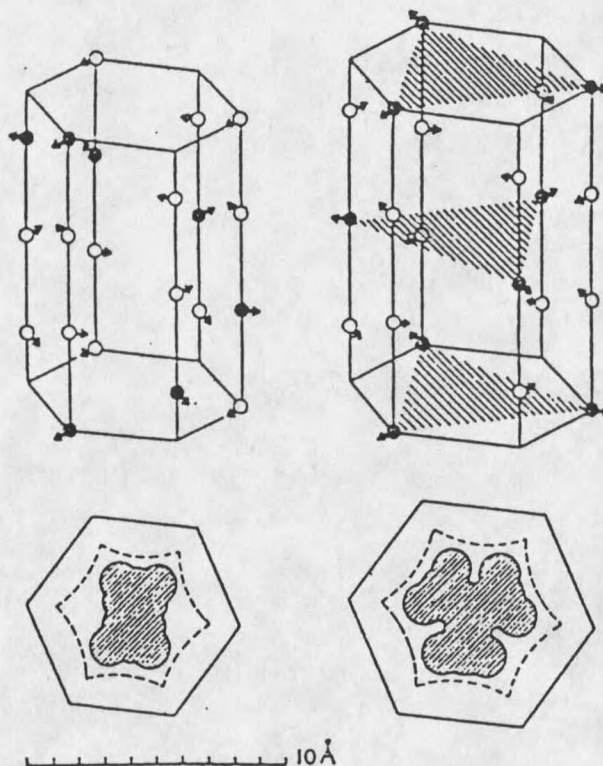


Figure 1

Lattice of urea (left) and thiourea (right) adducts

Top: Each circle represents a urea or thiourea molecule, the arrow points from the oxygen or sulfur atom towards the carbon atom. The filled circles represent a spiral of urea molecules in the urea lattice and the coplanar sulfur atoms in the thiourea lattice.

Bottom: cross section with included hydrocarbons
[reproduced from Schlenk (4)]

for the mole ratio (4). Guest molecules which can not "slide together" give mole ratios other than multiples of three. Based on measured crystal densities, he also determined that the favored mole ratios are always the results of this "sliding together" process and not due to empty gaps in the channel (4).

Schlenk reported that some hydrocarbons which by themselves do not form adducts will form adducts if certain adduct formers, termed inductors, are present (4). Included in these non-adduct formers which can be induced to adduct are benzene, toluene and the xylenes (6).

Gorton determined that 1,2,4 trichlorobenzene (TCB) will adduct by itself and serves as an inductor for the xylenes and other aromatics (12).

Welling reported that all the TCB isomers will form adducts with thiourea, and that only the 1,2,4 isomer of trimethylbenzene (TMB) will adduct by itself (3). X-ray diffractometer data was collected by Welling on a thiourea adduct containing a mixture of 1,2,3 TCB and 1,2,4 TMB. The space group was found to be $P2_1/c$ with unit cell parameters of $a=12.64$ A, $b=15.3$ A, $c=9.8$ A, $\alpha=\gamma=90$ and $\beta=113.85$. The Molecular Structure Corporation obtained a structure for the thiourea adduct of 1,2,4 TMB (3). A unit cell with parameters $a=12.3$ A, $b=15.1$ A, $c=10.0$ A, $\alpha=\gamma=90.0$, and

$\beta=112.7^\circ$ was found. Welling drew several conclusions concerning the interaction of the thiourea sulfur and hydrocarbon carbons from this structure. The evidence she found for the existence of a hydrogen bond is the shortening of the non-bonded distance between a C-H group and a sulfur atom. The Van der Waal distance, i.e. the sum of Van der Waal radii for C-H---S, is 4.08Å (13). Four distances between a C-H group and a sulfur atom were less than this Van der Waal distance. These distances are given in Table 3.

Table 3

Interatomic distances between sulfur and carbon in the 1,2,4 TMB and 1,2,3 TCB thiourea adduct

Atom 1	Atom 2	Distance
S1	C11	3.90Å
S1	C12	3.65Å
S1	C13	3.81Å
S2	C13	3.91Å

These distances are less than 4.08Å and may indicate hydrogen bond interactions. Angla suggested the presence of a strong coordination bond between the sulfur atom and the hydrocarbon molecule in the thiourea-carbon tetrachloride adduct (2).

An explanation for 1,3,5 TMB and 1,2,3 TMB not forming an adducts can be found in geometric considerations. From the drawing in Figure 2 it may be seen that 1,2,4 TMB can situate in the channel in such a manner that the methyl groups lie in the channel. However, 1,3,5 TMB and 1,2,3 TMB can not be situated such that all three methyl groups are in the channel (3).

Welling suggested some possible explanations of the action of adductors and non-adductors based on the electron configuration of the molecules (3). As mentioned earlier, benzene will not adduct with thiourea, but the isomers of TCB will. Therefore, the size or planar nature of the benzene molecule can not be responsible for inhibiting the formation of an adduct. In thiourea both the sulfur and nitrogen atoms have lone pairs of electrons. The electronic structure of benzene contains pi clouds which lie above and below the plane of the carbon atoms. These pi electrons are delocalized and form a "donut" of electron density. Welling suggested that the repulsion forces between the pi electrons of benzene and the lone pairs of electrons in nitrogen and sulfur are too great to allow the formation of the thiourea lattice. The chlorines of TCB must somehow influence the formation of the adduct. Welling asserted that the chlorine atoms are involved in hydrogen bonding.

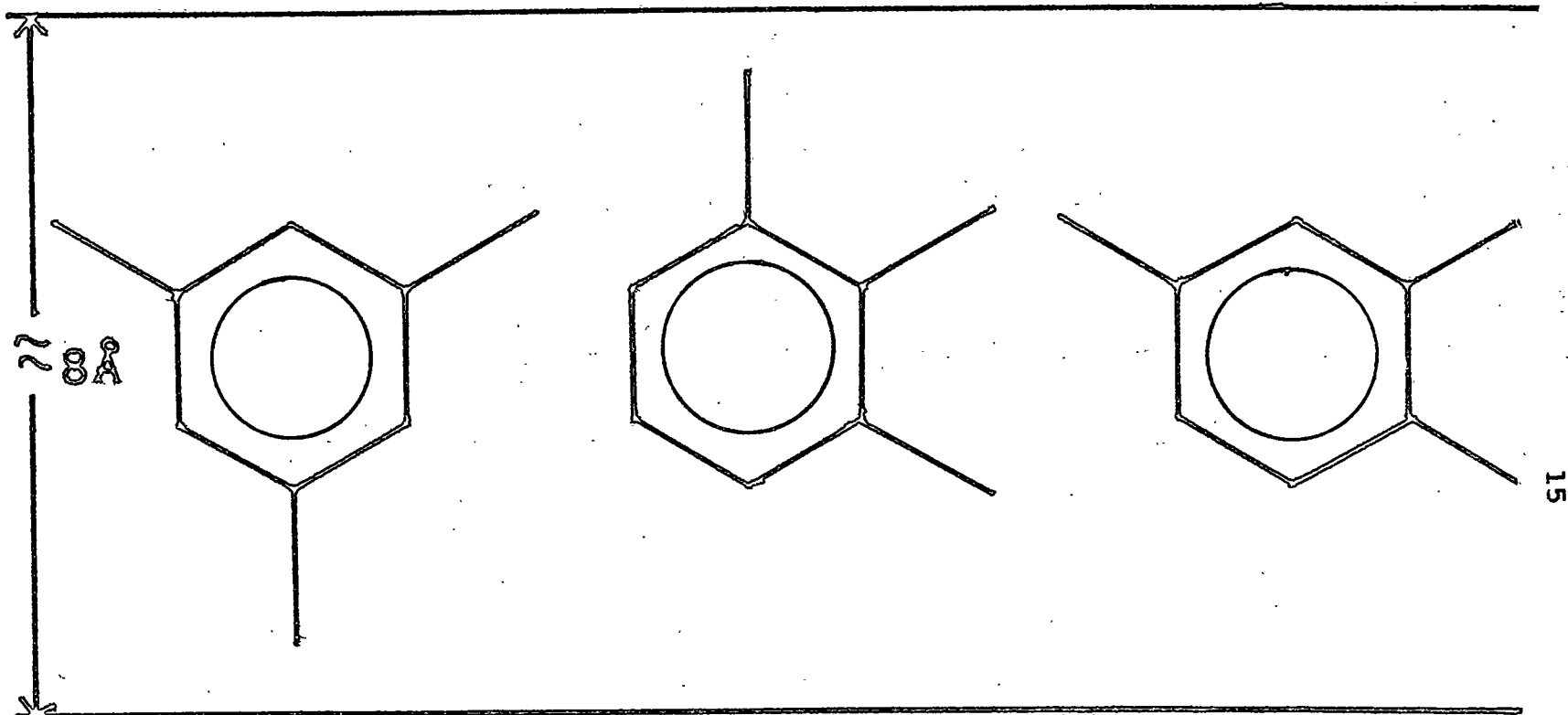


Figure 2

1,3,5 TMB, 1,2,3 TMB and 1,2,4 TMB in the channel
of a thiourea adduct

"Chlorine is an electronegative atom and it is recognized as a hydrogen bond acceptor. Chlorine is able to withdraw electron energy from the pi clouds around benzene and is receptive for hydrogen bonding with the N-H group in thiourea."

In related work Fait and Fitzgerald (14) determined the crystal structures for the cyclohexane-thiourea adduct and the carbon tetrachloride-thiourea adduct. The unit cell parameters reported for these structures are presented in Table 4. Both of these structures are in the space group $R\bar{3}m$, which is typical of non-aromatic adducts, and exhibit the honey-comb type channel structure formed from thiourea with the adduct molecule occupying the channel. The channel structure is illustrated in Figure 3 which is a stereoview of the carbon tetrachloride structure looking down the c-axis.

The thiourea positions were easily found in the refinement of both of these structures. More difficult was the determination of a model for the molecule in the channel. In Figure 3 the sulfur atom of the thiourea can be seen pointing into channel at the enclosed carbon tetrachloride molecule. This sulfur atom is hydrogen bonded to other thiourea atoms and is close enough to the channel molecule for Van der Waals interactions. Tables 5 and 6 present contact distances between the sulfur atom and

Table 4

Unit Cell Parameters for Cyclohexane and Carbon
Tetrachloride Adducts [from Fait and Fitzgerald
(14)] (all distances in Å, numbers in
parentheses are standard deviations)

Hydrocarbon Adducted with	A	B	C	α	β	γ	Space Group
Cyclohexane	15.708(1)	15.708(1)	12.431(2)	90.0	90.0	120.0	R3bar
CCl ₄	15.539(1)	15.539(1)	12.529(2)	90.0	90.0	120.0	R3bar

