The X-ray crystallographic structure study of the 1,2,4 trimethybenzene thiourea adduct and 1,2,4 trichlorobenzene thiourea adduct

by Thomas Albert Wick

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
Montana State University

Abstract:
Many hard-to-separate aromatic mixtures can be separated by adduct formation with thiourea. Thiourea adduction can be very selective even between aromatic isomers. In order to better understand the selectivity mechanism and the forces which hold thiourea complexes together, an x-ray crystallographic structure study was performed on two aromatic, thiourea adducts.

A diffractometer data set was collected on a 1,2,4 trichlorobenzene-thiourea adduct crystal and on a 1,2,4 trichlorobenzene—thiourea adduct crystal. Both adducts were solved in the space P21/c in a monoclinic unit cell with parameters of a = 10.037(2), b = 15.155(1), c = 12.255(1), &alpha = γ = 90.0°, β = 112.77°(3), and a = 9.779(1), b = 15.355(1), c = 12.293(2), α = ^gamma; = 90.0°, β = 111.85&degj(4) for the 1,2,4 trimethybenzene adduct and 1,2,4 trichlorobenzene adduct respectively. A disorder model for each adduct was proposed and the resultant R values were 0.0951 and 0.1053 for the 1,2,4 trichlorobenzene adduct and 1,2,4 trimethylbenzene adduct, respectively.

The general characteristics of these two structures are consistent with other similar thiourea adduct structures. The possibility of a hydrogen bond between the aromatic ring C-H group and the thiourea sulfur was found in both structures. From the non-bonded distances between the thiourea sulfur atoms and the disordered aromatic, evidence for a dipole-dipole interaction exists.

THE X-RAY CRYSTOLLOGRAPHIC STRUCTURE STUDY OF THE 1,2,4 TRIMETHYBENZENE THIOUREA ADDUCT AND 1,2,4, TRICHLOROBENZENE THIOUREA ADDUCT

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APPROVAL

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Thomas Albert Wick

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.

5-29-86
Date

J P McCandless
Chairperson, Graduate Committee

Approved for the Major Department

5-30-86
Date

John T. Sears
Head, Major Department

Approved for the College of Graduate Studies

June 4, 1986
Date

Henry L Parsons
Graduate Dean

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ABSTRACT

Many hard-to-separate aromatic mixtures can be separated by adduct formation with thiourea. Thiourea adduction can be very selective even between aromatic isomers. In order to better understand the selectivity mechanism and the forces which hold thiourea complexes together, an x-ray crystallographic structure study was performed on two aromatic, thiourea adducts.

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INTRODUCTION

Background

Frequently in industrial chemical processes mixtures of hard-to-separate aromatic compounds turnup. Since the compounds in these mixtures have similar physical and chemical properties, separation is often times difficult and economically poor. Although conventional separation techniques for these systems are diverse, they typically require large amounts of energy to effect a minimal degree of separation.

Distillation has been the standard technique for making such aromatic hydrocarbon separations, but in some cases it is impractical since the mixtures may pyrolize, may have close boiling isomers and/or form azeotropes. An alternative separation technique useful for aromatic, isomeric hyocarbon mixtures is extractive crystallization.

Extractive crystallization, by its analogy to the nonideal extractive distillation, is a selective process wherein a given compound preferentially forms an adduct crystal with another component thus effecting a separation (1). Adduct complexes are a class of non-stoichiometric compounds in which "guest" molecules are entrapped in channels or cagelike structures formed by "host" molecules. Adduct crystals will form only with suitable "guest" molecules since the spatial characteristics of the channel places structural constraints on the guest molecules which can be accommodated. When an adduct is decomposed, the "host" and the "guest" molecules are returned unchanged.

The most prevalent of "host" molecules are urea and thiourea. It is hypothesized that urea and thiourea form complexes easily because of their large dipole moment and zwitterion characteristics (1). Urea forms crystalline adducts with normal hydrocarbons, but usually not with branched or cyclic compounds unless the straight chain portion is sufficiently long enough. Thiourea forms channel adducts similar to the urea adducts, however, due to the larger sulfur atom the channel which entraps the "guest" is larger and thus can accommodate a larger "guest". On the other hand, a straight chain alkane would leave too much of the channel unfilled producing an unstable structure.

The hydrocarbons which can be adducted with thiourea include the branched paraffins, cyclohexyl-paraffins, certain chlorocompounds and some branched cyclic aldehydes, alcohols, napthalenes, and ketones (2). Recent research has shown that substituted aromatics can be complexed with thiourea. Substituted aromatics known to adduct are o-xlene, 1,2,4 trimethylbenzene, and the isomers of trichlorobenzene. Certain aromatics can be induced to adduct if an additional compound, referred to as an inductor, is present. The inductors' contribution to the complexing is not well understood, yet the inductor appears to be selective with regard to certain aromatics.

Numerous organic compounds have been separated by adduct formation with urea and thiourea by batch or continuous methods. The continuous method uses a fluidized, fixed or moving bed of urea or thiourea with which the organic components are brought into contact.

The adduct crystals are filtered or decanted, then decomposed usually by steam distillation or by heat.

Historical Review

The words complex and adduct came into common use during the formative years of synthetic organic chemistry to designate substances which do not appear to be held together by classical chemical bonds. These substances were designated by early German investigators as "Einschlussuerbindungen" or inclusion compounds. The discovery of urea adducts was made accidently in 1940 by Bengen while studying the action of urea on proteins in pasteurized milk. In these studies frothing and formation of an emulsion were causing difficulties, so Bengen added a small amount of n-octyl alcohol as a defrothing agent. Bengen observed the formation of long crystals at the interface of the liquid layers. On attempting to reproduce these crystals, Bengen discovered that they also form when a saturated aqueous urea solution was mixed with n-octanol. Further investigation extended the urea adduct formation to include higher alcohols, acids, n-paraffins, and other straight chained compounds (2).

Bengen's work came to Lloyd Fetterly's attention in the Technical Oil Mission publications of 1946. Fetterly was attempting to improve the octane ratings of gasoline by using a complexing agent which would readily react with the low octane branched paraffins. Although urea would not complex with these hydrocarbons, he discovered that thiourea would complex with the branched-chained paraffins as well as with naphthenic compounds, some ketones, carbon tetrachloride, and some other chloro compounds. His studies also showed complex formation with selenourea and tellurourea. Concurrently in 1947 Angla, in France, independently reported similar complexes between thiourea and organic compounds of the terpene, camphene, cyclohexane, and chloroparaffin classes (3).

In 1950 Redlick contributed to the current knowledge of thiourea channel adducts by conducting thermodynamic studies at equilibrium conditions. Using Gibbs free energy relationships and a chemical equilibrium equation, Redlich reported the composition and equilibrium constants for the decomposition of thiourea complexes of various isoparaffins, naphthenes and carbon tetrachloride. He concluded that equilibrium appeared to be that of a normal chemical reaction (4).

The indeterminate structure of the channel adducts prompted Smith (5) and Schlenk (6) to conduct x-ray analysis on urea and thiourea complexes in 1949. Smith examined a number of urea complexes of n-hyrdocarbons, alcohols, acids and esters of various chain length C_8-C_{50} by the powder method. Results indicated essentially identical powder patterns for all complexes. The extinctions and symmetry of the Weissenburg patterns established the space group as $C6_12$-D_62 or its enantiomorph $C6_52$-D_63 (See Appendix A). The unit cell for the complexes is hexagonal with lattice parameters a = 8.230 A and c = 11.005 A.

The urea molecules were shown to form three interpenetrating helical spirals with the hydrocarbon situated in the center. The urea molecules are held together by spirals of hydrogen bonds between an oxygen atom and a nitrogen atom of adjacent molecules turned 120^{o} with respect to one another. Each oxygen is hydrogen bonded to four nitrogen atoms and each nitrogen to two oxygen atoms. The hydrogen bonds, which are essentially coplanar with the urea molecules to which the nitrogens are attached, are of two types. The N....O distances are 2.93 A for the shorter and 3.03 A in length for the longer. The C-N-H...O bond angles are 136° and 116° respectively for the strong and weak bonds.

The hydrocarbons located inside the channel, are at the special positions (o,o,z) in a zigzag planar configuration with the long axis of the molecule parallel to the c-axis. The hydrocarbon molecules show a disorder parallel to the c-axis. Rotation of the hydrocarbon about the c-axis appears to cause this disorder.

Stability of channel adducts involves several physical and chemical phenomena. Pure urea forms tetragonal crystals, whereas urea adducts are hexagonal. The bond distances between the two forms are in Table 1.

Table 1. Bond distances (A) in urea.

Urea-Hydrocarbon Complexes		Pure Tetragonal Urea	
C-O	1.28	C-O	1.25
C-N	1.33	C-N	1.37
N-H...O	2.93 A	N-H...O	2.99 A
N-H...O	3.03 A	N-H...O	3.03 A

The shortening of the N-H...O bond yields a lower energy value which indicates more stability in the hexagonal vs tetragonal form (9). The complexes are further stabilized by the urea-hydrocarbon van der Waals bonds. Schlenk calculates a value of 2.8 kcal per CH_2 group in urea complexes. Smith, however, refuted any unusually strong interaction between the hydrocarbons and the urea such as that indicated by Schlenk. Smith suggests that the closest possible approach between a carbon atom of the hydrocarbon and an oxygen atom of the urea is approximately 4.1 A which is as large as or larger than normal van der Waals distances for these atoms.

Fetterly (2) points out a new concept that a stronger hydrogen bond can exist only when it is supported by an otherwise inert surface (i.e., the channel hydrocarbon) capable of exerting only weak dispersion forces. Without the presence of a hydrocarbon, urea or thiourea complexes cannot exist. Fetterly referred to these additionally stabilized bonds as "supported hydrogen bonds." It was this phenomenon that Fetterly claimed stabilized urea and thiourea adducts.

Another factor that may contribute to the stability of the complexes is that the van der Waals forces in the tetragonal urea may be less than normal because of the relatively open structure (Figure 1), while those in the complex would appear to be normal (5). This is also indicated by the smaller volume occupied by the complex compared to the same number of urea molecules and guest hydrocarbon molecules in their standard, pure crystalline states.

The complexes of non-aromatic thiourea discovered by Fetterly and Angla are similar to urea complexes in almost every respect. The arrangement of thiourea molecules in the adducts is rhombohedral, forming a pseudohexagonal but similar cell to that of urea complexes.

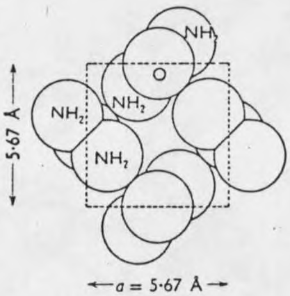


Figure 1. Tetragonal urea showing the relatively open structure.

There are 18 thiourea molecules per unit cell with space group R3 2/C and a = b = 15.8 A, c = 12.5 A along the channel length (3). As with urea, the crystal structure of thiourea in an adduct is different from that of the pure reagent. Pure reagent thiourea crystalizes in space group Pbnm and is orthorhombic. The unit cell constants of the thiourea adducts apparently vary slightly with the nature of the adducted hydrocarbon, hence, so will the channel dimensions vary slightly.

The larger size of the sulfur atom in thiourea, compared with the oxygen in urea, results in a channel of larger dimensions capable of adducting larger cross-sectional guest hydrocarbons. In Figure 2 the cross-sections show the thiourea adduct schematically containing the larger guest molecule. The distance between two molecules lying one above another is 4.2 A, and the edge length of the cell is 5.4 A, these values compare with 3.7 A, and 4.8 A respectively for the urea adduct.

Figure 2 shows only the oxygen or sulfur atoms with arrows pointing toward the carbons. The dotted lines in the urea hexagonal prism connect oxygen atoms of the same elementary cell and indicate the helical structure. The three shaded regions in the thiourea adduct represent planes formed by three coplaner sulfur atoms pointing directly into the channel. Schlenk suggested that because of the optimal positions of the three coplaner thiourea molecules and their strong dipole moments that these planes were regions of maximum attraction (6). Coplaner sulfur atoms occur every third sulfur along an edge and since each atom is approximate 4.2 A apart, the distance between planes is 12.5 A which is the c-axis unit cell dimensions.

A number of researchers conducted composition studies on urea and thiourea complexes. In urea and thiorea complexes the ratio of urea or thiourea molecules to guest hydrocarbon molecules increases linearly with the length of the guest hydrocarbon (Table 2). Exception to this relationship is with guest hydrocarbons which exhibit what Schlenk referred to as compressibility. Table 2 uses w-w'- methylene bridged dicyclohexyls as an example of compressible guest hydrocarbons.

Schlenk (6) recognized that dicyclohexylmethane, 1, 2 dicyclohexylethane and 1, 3 dicyclohexylpropane showed an almost constant mole ratio of 6:1. Their x-ray patterns shows a compression of the slender paraffinic portion of the guest molecule in the channel. In this way several w,w - dicyclohexyl derivatives can fit into the

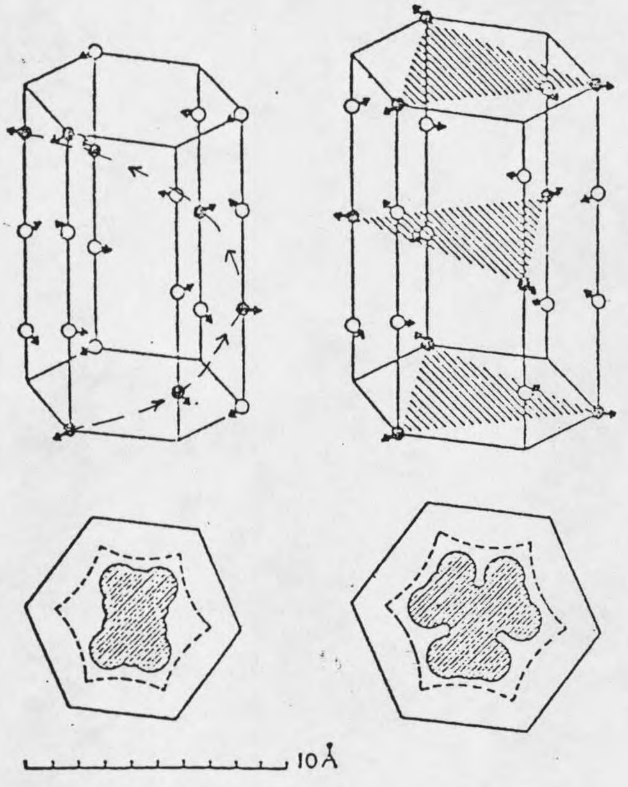
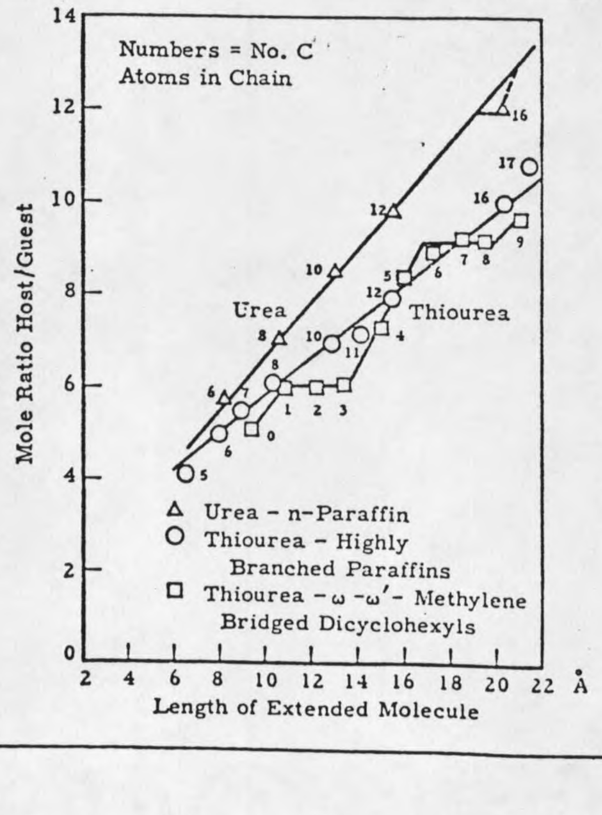


Figure 2. Lattice of urea (left) and thiourea (right) adducts. Top: each circle represents a urea or thiourea molecule, the arrow points from the oxygen or carbon atom toward the sulfur atom. Bottom: cross-section with included hydrocarbons [reproduced from Schlenk (6)].

same channel space. Thus, if the fully extended length of the guest hydrocarbon exceeds an integral multiple of c/2 only slightly, there is a tendency for the enclosed molecule to take up a somewhat less extended form whenever possible to fit the repeating half unit of the thiourea complex. In this way the terminal cyclohexyl rings coincide with the zones of maximum attraction (12). Since only one site of maximum attraction occurs per unit cell, molecule ratios of muliples of three (i.e. 3:1, 6:1, 9:1 etc) will preferentially occur when the guest hydrocarbon can compress. In Table 2 the plateaus at molecule ratio 6:1 and 9:1 exhibit this behavior. Guest molecules which cannot compress will form complexes of multiples other than three.

Table 2. Lengths of the quest hydrocarbon plotted against the molar ratio thiourea: guest for compressible and noncompressible guest.

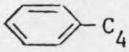
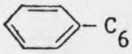
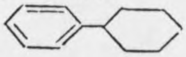
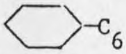
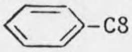
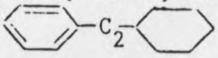
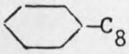
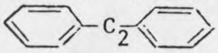
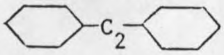
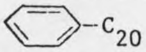
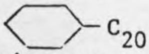
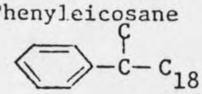
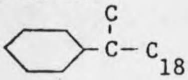
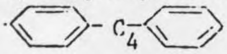
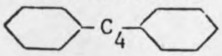


McLaughlin compiled a comparison list (Table 3) of organics, of similar size and shape, that will or will not adduct with thiourea. Although the dimension of the benzoid ring is very close to those of the cyclohexyl ring, no adduction occurs. This suggests that adduction with thiourea requires the guest hydrocarbon to have other properties besides the appropriate cross-sectional dimensions.

Some compounds which are non adducting by themselves can be induced to form a thiourea complex when mixed with certain adduct formers called "inductors". Examples of induced compounds are toluene, benzene, the xylenes, neptane, decane, dipentene, and 1, 3 - dimethycyclohexane. Some examples of inductors are, cyclohexane, dicyclohexyl, 2, 2, 4 trimethylpentane and decahydronaphtholene (2).

McCandless (10) reported the inductors which would adduct C_8 and C_9 alkylbenzenes. His work exemplified the ability of extractive crystallization with thiourea to be an effective separation technique for aromatic isomers and aromatics of close boiling points. For example CCl_4 as an inductor exhibited a selectivity of ethylbenzene > o-xylene > p-xylene > m-xylene while the use of 1,2,4 trichlorobenzene (inductor) resulted in a selectivity of o-xylene > p-xylene > m-xylene > ethylbenzene. With the C_9 alklybenzenes, CCl_4 as an inductor was selective for n-propylbenzene while 1,2,4 trichlorbenzene was selective for 1,2,4 trimethybenzene. Similarly o-xylene and 1,2,4 trimethybenzene exhibited the same selectivity as 1,2,4 trichlorobenzene when used with mixtures of the C_9 and C_8 aromatics, respectively. All of the inductors mentioned above also form complexes alone.

Table 3. Compound which form adducts with thiourea compared to similar compounds which do not form adducts.

Nonadducting	Adducting	Adducting
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 

*Reproduced from Mandelcorn (2)

Welling measured the unit cell dimensions of the binary 1,2,4 TCB/1,2,4 TMB thiourea adduct and found a=12.64A, b=15.3A, c=9.8A, α = γ = 90.0^{o} and β = 113.85^{o}. Welling also enlisted the Molecular Structure Corporation to obtain a structure for the 1,2,4 TMB thiourea adduct. Unit cell dimensions obtained were a=12.3A, b=15.1A, c=10.0A, α = γ =90.0, and β =112.7^{o} (12). Due to the disordered arrangement from a translational view as well as through the inversion center, a conclusive structure was not obtained from the Molecular Structure Corporation. However, Welling did postulate some ideas about the thiourea lattice and 1,2,4 TMB interactions from intermolecular distances.

Initially Welling reasoned that benzene did not adduct because the pi clouds, which lie both above and below the plane of the carbon atoms, form a repulsive force with the lone pairs of electrons on the nitrogen and sulfur of thiourea. With this idea Welling speculated that 1,2,4 TMB adducted because of an interaction between the methyl groups and the thiourea lattice. The isomers of 1,2,4 TMB (ie 1,3,5 TMB and 1,2,3 TMB) did not adduct indicating a steric hinderance toward adduction. The methyl groups on 1,3,5 trimethylbenzene are symmetrically dispersed about the benzene ring and the methyl groups on 1,2,3 trimethylbenzene are concentrated to one side of the ring. Both isomers are larger in diameter than that permitted by the thiourea lattice and hence no adduction occurs.

In 1,2,4 TMB the benzene ring increases the electron density of the carbon atom on the methyl group (13). The methyl groups become slightly acidic, or partially positive, through this resonance effect and will induce weak hydrogen bonding with the sulfur atom in the thiourea molecules. Welling reasoned that if a hydrogen bond were to be possible, the distance between the C-H group and sulfurs must be closer than the non-bonded van der waal distance. Since the covalent radii for a C-H group is 1.08 A, the van der Waals radii for hydrogen is 1.15 A, and the van der Waals radii for sulfur is 1.85 A, the non-bonded distance is the sum of these radii, or 4.08 A. The Molecular Structure Corporation reported the observed contacts between sulfur and carbon. These distances are tabulated in Table 4. All of the distances are less than the non-bonded distance (4.08 A) and thus hydrogen bonding is a possibility (12).

Table 4. Interatomic distances between sulfur and carbon in the 1,2,4 TMB-thiourea adduct.

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

At Montana State University researchers Fait and Spinti, et al, have conducted structural analysis on non-aromatic isostructural thiourea adducts. Fait reproduced Lennes' crystal structure for the cyclohexane-thiourea adduct and independently determined the crystal structure of the carbon tetrachloride-thiourea adduct and the bicyclo (2.2.2) octane-thiourea adduct. Spinti obtained a crystal structure for the cis-paramenthane thiourea adduct. All three complexes crystallize in the rhombohedral space group, R3bar, as is characteristic for non-aromatic complexes. In addition, the honeycomb shaped thiourea lattice formed with all three complexes. The lattice parameters are tabulated in Table 5. The guest hydrocarbon was disordered translationaly as well as around the axis of symmetry in all three adducts. Figure 3 shows the thiourea lattice with the guest hydrocarbon, cis-paramenthane, (Fig. 4) disordered in the channel. Fait reported sulfur atoms pointing into the channel and hydrogen bonded to other thiourea molecules. He concluded that dipole-dipole interactions between the three coplaner thiourea sulfurs and the CCl_4 carbon and between the three coplaner thiourea sulfers and cyclohexane hydrogens are responsible for binding of the substrate hydrocarbon in these complexes. Fait recognized that the sulfur-carbon double bond distance for thiourea in these non-aromatic complexes was lengthed in comparison with that of pure thiourea. Table 6 shows the magnitude of these bond distances. If a linear relationship between bond strength and the c = s bond distance is assumed then the conclusion which can be drawn is that the dipole interaction between the coplaner sulfurs and the guest hydrocarbon is stronger than the hydrogen bonding interaction in pure thiourea.

Table 5. Unit cell parameters for cis-paramenthane, cyclohexane and carbon tetrachloride adducts. All distances and angstroms.

Hydrocarbon Adducted with	A	B	C	α	γ	β	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
Cis-paramenthane	15.935(1)	15.935(1)	12.489(2)	90.0	90.0	120.0	R3bar

Table 6. Sulfur-carbon double bond distances in the thiourea for various non-aromatic adducts.

Crystal	Thiourea Sulfer = Carbon Bond Distance
Cydohexane-Thiourea Adduct	1.725 (9)
CCl_4-Thiourea Adduct	1.744 (8)
Bicyclo [2.2.2] Octane Thiourea Urea Adduct	1.731 (5)
Pure Thiourea	1.708 (5)

Research Objectives

The purpose of this research was to continue the investigation of the selectivity mechanism of aromatic thiourea adducts begun at Montana State University. This objective would be facilitated by:

1. Obtaining a crystal structure of a 1,2,4 TMB-thiourea complex using a more correct model than that employed by Welling and the Molecular Structure Corporation.
2. Obtaining a crystal structure of a 1,2,4, Trichlorobenzene-thiourea adduct in order that the heavier chlorine atoms might resolve the disorder problem associated with the guest hydrocarbons in thiourea complexes.
3. From the intermolecular distances and positions yielded from these structures, ascertain the interactive forces between the thiourea honeycomb lattice and an aromatic guest hydrocarbon.

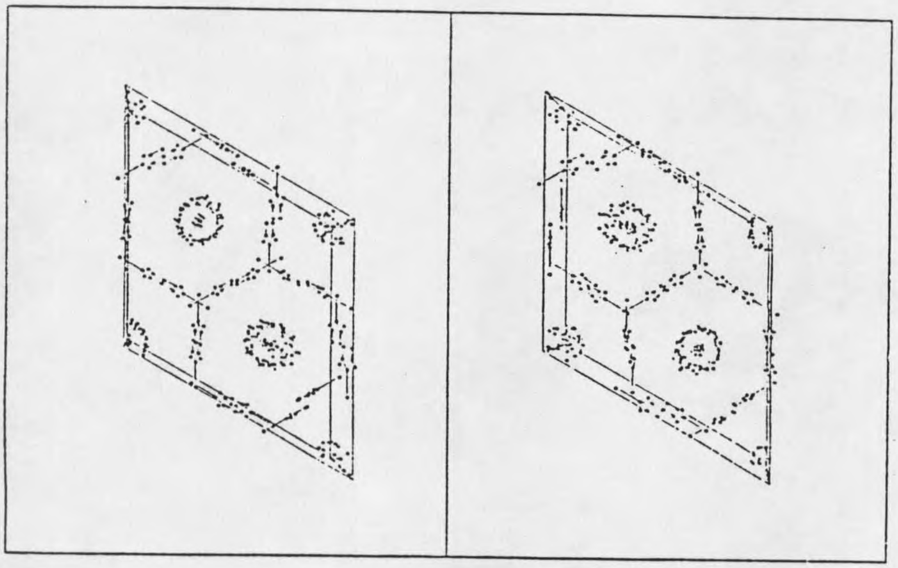


Figure 3. Cis para-menthane adduct viewed down the a-c diagonal.

EXPERIMENTAL

Crystal Preparation

The preparation of 1,2,4 trimethlybenzene-thiourea adducts and 1,2,4 trichlorobenzene-thiourea adducts has already been reported (10,11,12). However, an alternative technique was employed to avoid twinning and enhance slow crystal growth. A 20 ml saturated solution of pure reagent thiourea and methanol was heated in a constant temperature bath of 40^{o}C. Approximately three to four milliliters of 1,2,4 TMB or 1,2,4 TCB was added to this solution and the mixture was sealed to avoid evaporation. After one-half hour the mixture was taken from the 40^{o}C bath and placed in a 17^{o}C constant temperature bath. Crystals from each aromatic system formed within 24 hours. The adduct crystals formed were long, clear, hexagonal, and needle-like. Any white, flat or plate-like crystals were known to be pure thiourea crystals and were avoided when crystals were selected for x-ray analysis.

Crystal Analysis

To ensure the reagent 1,2,4 TCB was not contaminated with its isomers, a distillation was performed. At the time of distillation the barometric pressure was 638 mm Hg and the reflux ratio was 20:1. In addtion, both adduct systems were analyzed by an elemental analysis and by using a Varion Aerograph Series 1400 Gas Chromatograph.

Elemental analysis was conducted on the 1,2,4 TCB adduct 1,2,4 TMB adduct and pure reagent thiourea. The instrument employed was a Carlo Erba Strumentazione Elemental Analyzer.

Crystals were prepared for both analyses by vacuum filtering crystals, then placing them on filter paper to air dry for one hour. If crystals are exposed to air for any extended length of time the guest hydrocarbon will evaporate and the adduct will decompose. Crystals to be analyzed with the gas chromatograph were then placed in a minimum amount of boiling, distilled water. The thiourea dissolved in the water layer and the 1,2,4 TMB or 1,2,4 TCB formed a separate, immiscible layer. The organic layer and the aqueous layer were separated with a separatory funnel. The organic cut was analyzed with the Varion Gas Chromatograph using a 5% diisodecyphthalate and 5% bentone 34 on Chromosorb W column at 150° C. The carrier gas used was helium. Pure reagent 1,2,4 TMB and 1,2,4 TCB were analyzed with the gas chromatograph to compare as standards.

The dried crystals to be analyzed with the elemental analyzer were placed in small silver capsules and sealed with pliers. Each capsule was placed in a electrobalance which measured to the nearest 10^{-4}mg. To ensure that the capsule was sealed and not losing weight, due to evaporation of the 1,2,4 TMB or 1,2,4 TCB, the weight was monitored for 5 minutes. If in that time no change in weight was recorded, the capsule was removed from the balance and placed in the analyzer. Cicloesanone and Sulfanamide were used as the standards. Weight percentages of carbon, nitrogen and hydrogen were measured for each sample.

Adduct Density

The density of an adduct was determined by suspending the adduct in a mixture of miscible liquids, one more dense than the adduct and one less dense. The density of the solution which is in gravity equilibrium with the adduct is also the density of the adduct (21). In the case of 1,2,4 TCB a medium of carbon tetrachloride and methanol was used to suspend the adducts and for the 1,2,4 TMB system the medium used composed of heptane and 1,2,4 trichlorobenzene. Once the crystals would neither sink nor float in the medium, a known volume was weighed and the density calculated. The densities were 1.49 g/ml and 1.19 g/ml for the 1,2,4, TCB adduct and 1,2,4 TMB adduct respectively.

Crystal Mounting

Selecting an appropriate crystal for x-ray analysis required placing crystals on a microscope slide and positioning the slide under a dissecting microscope. Ample room was allowed for the crystals to be cut or fragmented along their length. Crystals were cut or fragmented to the appropriate size using a sharp razor blade or dissecting scalpel. Once a crystal fragment of suitable size and shape was selected, a glass fiber dipped in adhesive Paratone-N was used to transport the crystal from the microscope slide to a low lead glass capillary tube of approximately 0.8 mm in diameter. Care was taken not to choose pure thiourea crystals which might have crystalized out of the mother liquor.

The capillaries were sealed by heat or glue to prevent air exposure from decomposing the crystal. To check for twinning (multiple crystal growth), the crystals were examined under polarized light. Crystals which extinguished upon rotation between crossed nickle prisms were used for x-ray analysis. The 1,2,4 TMB adduct crystal used for data collection was cylindrical in shape measuring 0.6 mm in diameter and 0.8 mm in length. The 1,2,4 TCB adduct crystal was also cylindrical in shape and had dimensions 0.7 mm in diameter and length of 0.9 mm.

Photographic Film Studies

A Weissenburg camera was employed to check crystal quality and estimate unit cell dimensions. The radiation source used was copper with a nickel filter. Weissenburg photographs taken for a deteriorated adduct would show few, if any, layer lines and those lines which were present would contain indefinite spots. Once a suitable crystal was obtained, oscillation, zero level, first level, and second level photographs were collected to determine approximate unit cell dimensions.

Numerous Buerger Precession photographs were taken for the 1,2,4 TCB complex. These photographs were expected to provide support for, as well as clarification of, the unit cell dimensions. Problems were encountered which involved the alignment of the crystal for precession photographs and this method was abandoned since the photographs were not necessary to proceed with the diffractometer data collection.

Diffractometer Data Collection

Intensity data for both adduct systems were collected on a Nicolet R3mE automatic four circle diffractometer using the omega scan technique with the 1,2,4 TCB complex and the theta-two-theta scanning technique with the 1,2,4 TMB complex. The x-ray source used was MoK_2 radiation of λ = 0.71069 A, and monochromated with a graphite crystal monochromator. Both data sets were collected at room temperature. Throughout the course of the data collection three standard reflections were measured every one hundred reflections. There was no decrease in the intensity of these standards over the course of the data collection. For instance, the decrease in the average value of these standards was about 7% by the end of the data collection for the 1,2,4 TMB complex. Al intensities were corrected for the changes in the standards. Lattice parameters for the 1,2,4 TCB complex were obtained from the least squares fit of 20 centered reflections for which $25^o<2\theta<35^o$. For the 1,2,4 trimethylbenzene thiourea complex the same procedure was followed using 25 centered reflections with $28^o<2\theta<31^o$. The data collected on each complex ranged from 3^o to 50^o on 2θ. Asmuithal adsorption correction data was taken for both complexes.

For the 1,2,4 TMB complex the linear absorption coefficient, μ (MoK_2) was 4.01 cm^{-1} and no correction was made for absorption. For the 1,2,4 TCB complex, μ (MoK_2) = 8.89 $cm^{-1}$and an empirical absorption correction was made to the intensity data. The two data sets were reduced in the usual manner with appropriate Lorentz and polarization corrections. Scattering factors for Cl,S,O,N,C and H and anomolous scattering terms for all types except H were taken from the International Tables for X-ray Crystallography (18); all atoms were assumed to be in the zero ionization state.

For the 1,2,4 TCB-Thiourea complex, 3397 intensities collected yielded 1610 observed reflections. The data set for the 1,2,4 TMB-Thiourea complex had 3161 intensities collected of which 1536 were observed reflections. Criterion for observed reflections was $I > 3\sigma$. The data sets for both complexes reveal the monoclinic primitive lattice. In addition, both sets showed the following extinctions in Table 7.

Table 7. Extinctions and associated symmetries of the 1,2,4 TMB-thiourea complex and the 1,2,4 TCB-thiourea complex.

Reflections Absent	Symmetry Indicated
UOO	
UOG	n glide perpendicular
UOU	to b
OUO	2 fold screw axis on b

From these extinctions the space group P21/c was determined for both structures.

A least squares fit of 25 centered reflections produced the unit cell dimension of a = 10.037 A, b = 15.155 A, c = 12.255 A, β = 112.77°, and a = 9.779 A, b = 15,355 A, c = 12.293 A, β = 111.85° for the 1,2,4 TMB-thiourea complex and the 1,2,4 TCB-thiourea complex respectively.

Solution of Structure and Refinement

The 1,2,4 TCB complex was solved initially by direct methods. Since the two complexes are isostructural with respect to the thiourea honeycomb lattice, sulfur positions from the 1,2,4 TCB complex were used for the initial phasing of the 1,2,4 TMB-thiourea complex. Once the sulfur positions were found, the thiourea nitrogens and carbon appeared on the difference maps. These atoms, along with any other strong peaks, were added to a model and the model's structure factors were compared to the observed structure factors. A resultant R value was obtained and if the R value decreased, the peaks were left in the model. At this point the thiourea positions were well-defined, yet the channel atoms were disordered.

Refinement for both complexes was done using a block cascade least-squares refinement program where the minimization function;

$$M = \sum \text{weight } (|\text{Fobs}|-|\text{Fcalc}|)^2$$

used to refine 101 parameters in each full matrix block. Fobs was the observed structure factor and Fcalc was the calculated structure factor (22).

The thiourea molecules were well-behaved and thus a model was easily fit to the thiourea lattice. Once the carbon, sulfur and nitrogen atoms of the thiourea were well defined, hydrogen atoms of the thiourea began to appear on the difference maps and the thiourea molecules were refined anistropically.

The 1,2,4 TMB or 1,2,4 TCB remained disordered in the channel and were refined isotropically. In the final refinement the weighting factor used was

Weight 1/[sigma**2(F) + (.0004F*F)].

The 1,2,4 TMB-thiourea structure refined to R = .1053, Rw = .0911, Rg = .0990, Rm = .0990, and goodness of fit = 2.399. The 1,2,4 TCB-thiourea structure with the two ring disordered model refined to R = .0951, Rw = .0927, Rg = .1061, Rm = .1061, and goodness of fit = 2.650. Without the models, both structures refined to about R = 0.15.

RESULTS AND DISCUSSION

Discussion of X-ray Crystallography

An ideal crystalline substance is a homogeneous solid in which the atomic or molecular arrangement repeats by translation in three dimensions; the repeat distance and direction can be described by a three dimensional coordinate system. A crystal is composed of atoms oscillating about regular positioning of a lattice, repeating in accordance with the crystal system and symmetry (26). If x-rays are passed through a crystal the incident beam is diffracted by the electrons of the atoms according to Bragg's law of diffraction;

$$n\lambda = 2d\sin\theta$$

n = (1,2,3,4, . . .)
λ = wavelength of incident radiation
d = distance between reflecting planes
θ = angle between the incident or reflecting surface

The intensity and coordinates of the reflecting or diffracted radiation are collected by the diffractometer using a radiation counter. The intensity of a diffracted wave is dependent upon the atomic position and the atomic scattering factor, which is a function of the number of electrons in the atom. Furthermore, since changes in temperature of crystals affects the thermal vibrations of the atoms, the intensities must be corrected for this temperature effect. In general the greater the vibrations the more the intensities will be lowered.

The intensities of the reflections from the diffracted x-rays are directly obtainable from a radiation counter; however, the phases of the reflections are not directly obtainable, yet they are essential for crystal structure determination. Crystollographers have shown that the wave scattered by a crystal can be characterized by a quantity, F_{hkl}, referred to as the structure factor (23). More generally, the structure factor for any given configuration of matter is the ratio of the amplitude of the wave scattered by all the matter in that configuration in any direction to that scattered by a single electron under corresponding conditions. Thus, following this definition, the structure factor of an electron is always unity (24). The amplitude of a scattered wave is proportional to the intensity, only after scaling, Lorentz-Polarization corrections, absorbtion and other comperical corrections are applied to the intensity. Mathematically:

$$I_{hkl\ cal} = (F_{hkl\ cal})^2$$

$$F_{hkl} = \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)}$$

or,

$$F_{hkl} = \sum_j f_j e^{i\phi_j}$$

where I_{hkl} = intensity of nkl reflection

$$\left.\begin{array}{l} x_j \\ y_j \\ z_j \end{array}\right. = \text{fractional coordinators}$$

f_j = scattering power of an atom at angle 0

The scattering power of an atom is tabulated in the literature for all elements. The term Θ, is referred to as the phase of the reflected wave. Each F_{hkl} is complex; that is, it is characterized by both a magnitude, $1F_{hkl}1$, and a phase Θ_{hkl}. The magnitude can be experimentally observed but, as mentioned previously, the phase cannot (25).

If, in studying the arrangement of atoms in a given crystal a particular model is proposed, the set of F_{hkl}'s of the model can be computed. The test for correctness of a crystal-structure model to be correct is that the set of structure factors computed, $F_{hkl\ calc}$, match the observed structure factors, $F_{hkl\ obs}$. It is, however, possible to obtain a good agreement with an incorrect structure. This calculation is greatly simplified by fast computers.

The ultimate goal in the determination of a crystal's structure is finding the positions of all the atoms in the unit cell. These atomic positions are not found directly but are deduced from the electron density. Atomic positions are found where the electron density is at a maximum. The electron density, ρ (x,y,z), is computed using the equation:

$$\rho(x,y,z) = 1/V^{*}\sum\sum\sum F_{hkl}e^{-2\pi i(hx+ky+lz)}$$

where V = volume
Fhkl = structure factor of hkl reflection
x
y = fractional coordinates
z

Thus, once structure factors are determined, the electron density can be computed using Fourier synthesis. The $F_{hkl\ calc}$ and $F_{hkl\ obs}$ determined are refined using least squares calculations. The measure used to quantify the agreement between the model and the actual data is the R value. The R value equation used for the 1,2,4 TMB complex and the 1,2,4 TCB complex was:

$$R = \frac{\Sigma||F_o|-|F_c||}{\Sigma|F_o|},$$

$$R_w = \frac{\Sigma[||F_o|-|F_c||*(\text{weight})^{1/2}]}{\Sigma[F_o*(\text{weight})^{1/2}]}$$

$$R_g = \frac{[\Sigma(\text{weight}*[||F_o|-|F_c||]^2)]^{1/2}}{\Sigma[\text{weight}*F_o^2]}$$

R_m = R_g (calculated for the scale factor which minimizes R_g) (22).

Conventionally, R values less than about 0.07 reveal that the model has "solved" the crystal structure, although technically it only means that the model fits the data within reasonable agreement. To claim the model represents the true crystal structure, the agreement (R value) between F_{obs} and F_{calc} must be acceptable and the model must adhere to chemical and physical laws.

Aromatic-Thiourea Complexes

The Molecular Structure Corporation's x-ray analysis of 1,2,4 TMB-thiourea complex was unable to resolve the disorder of the 1,2,4 TMB in the channel. This motivated a new structure determination using a different model solution. Furthermore, it was hypothesized that if the methyl groups in 1,2,4 trimethylbenzene were replaced with chlorines, forming 1,2,4 trichlorobenzene, that these heavier chlorine atoms would appear more defined in an x-ray analysis. If the chlorine atoms were more defined in an x-ray data set, a correct model would be assembled easier.

From floatability the densities of 1,2,4 TMB-thiourea and 1,2,4 TCB-thiourea were 1.19 g/ml and 1.49 g/ml respectively. The elemental analysis listed in Appendix B proved the thiourea to be of pure reagent grade and a balance on nitrogen showed the mole ratio of thiourea to aromatic to be 4.38 and 3.55 for 1,2,4 TMB-Thiourea and 1,2,4 TCB-Thiourea respectively. These mole ratios were confirmed by the density measurements which yielded mole ratios of 4.40 and 3.55 for the 1,2,4 TMB-Thiourea and 1,2,4 TCB-Thiourea respectively. The distillation of 1,2,4 TCB and the gas chromotography analysis proved the adducts to contain only the pure reagents (i.e. no isomeric impurities).

Additional structures studied for comparison in this work are listed in Table 8. As can be seen, the non-aromatics crystallize in the same space group R3bar and have similar cell dimensions. The adduct containing a 50 mole percent of both 1,2,4 TCB and 1,2,4 TMB crystallizes in the same space group as the 1,2,4 TMB-thiourea and 1,2,4 TCB-thiourea complexes and has approximately the same cell dimensions. This change in space group between aromatic and non-aromatic adducts suggests that there is a fundamental change in the thiourea channel shape. This change indicates a possible different kind of interaction between the aromatic and the thiourea lattice than that between non-aromatics and thiourea.

The two adduct systems were proved to be isostructural when the thiourea positions from the 1,2,4 TCB-thiourea were successfully used for the initial phasing for the thiourea positions in the 1,2,4 trimethylbenzene-thiourea adduct. Figures 4 and 5 exhibit the similarities between both complexes' thiourea lattice. The structures show a pseudo hexagonal lattice with distorted channel walls. The view is down the a-c diagonal. Both structures have very similar atomic positions for the thiourea molecules. The graphics software in the SHELXTL package allowed for interatomic distances between bonded and non-bonded atoms to be found (22).

The graphics program showed each sulfur atom to be hydrogen bonded to NH_2 groups on four adjacent thiourea molecules. This is illustrated in Figures 6, 7, and 8 where the hydrogen bonding scheme in

Table 8. Structural data for related thiourea complexes. All distances and angstroms.

Hydrocarbon Adducted with	A	B	C	α	β	γ	Space Group	DENSITY (g/cm^3)
Cyclohexane	15.708(1)	15.708(1)	12.431(2)	90.0	90.0	120.0	R3bar	1.138
CCl_4	15.539(1)	15.539(1)	12.529(2)	90.0	90.0	120.0	R3bar	1.415
cis para-menthane	15.935(2)	15.935(2)	12.489(2)	90.0	90.0	120.0	R3bar	1.16
1,2,3 TCB and 1,2,4 TMB	12.64	15.3	9.8	90.0	113.8	90.0	$P2_1/c$	1.27
1,2,4 TCB and 1,2,3 TMB							$P2_1/c$	1.3
1,2,4 TCB	9.779(1)	15.355(1)	12.293(2)	90.0	111.85	90.0	$P2_1/c$	1.49
1,2,4 TMB	12.3 (1)	15.1 (1)	10.0 (2)	90.0	112.7	90.0	$P2_1/c$	1.19
1,2,4 TCB and 1,2,4 TMB	9.886(7)	15.245(8)	12.313(6)	90.0	112.48(4)	90.0	$P2_1/c$	1.28

the thiourea network of the 1,2,4 TMB-thiourea adduct is shown. The four hydrogen bonds, denoted as dotted or dashed lines, are of lengths 3.314 A, 3.402 A, 3.454 A, and 3.452 A. The corresponding lengths for the 1,2,4 TCB-thiourea adduct are 3.433 A, 3.348 A, 3.446 A, and 3.408 A. At room temperature pure crystalline thiourea has three sulfur-nitrogen hydrogen bonds of 3.526 A, 3.394 A, and 3.696 A in length (15). The shortening of these hydrogen bonds in the complexes indicates a lower energy state and correspondingly a greater stability. Although Smith contends that compacting of the adduct structures is solely responsible for holding the adduct together, a review of Table 2 suggests other factors seem at work. For example, evidence of this is the fact that cyclohexane adducts, but benzene does not.

Schlenk suggests a zone of maximum attraction in each unit cell, corresponding to three coplaner sulfur atoms (see Figure 2). These zones are evident in both the 1,2,4 TCB-thiourea adduct and the 1,2,4 TMB-thiourea adduct. Figure 9 shows three coplaner sulfur in the 1,2,4 TMB-thiourea adduct, pointing directly into the channel exhibiting a zone of maximum attraction. The three thioureas do not form an equilateral triangle, but instead are slightly distorted about the a-c diagonal.

The thiourea lattice in each complex is by and large responsible for the space group symmetry and therefore the positions and intermolecular distances and angles are nearly identical for both structures. Figure 10 shows the three coplaner sulfur atoms for the 1,2,4 TCB-thiourea adduct with open lines forming a triangle. The

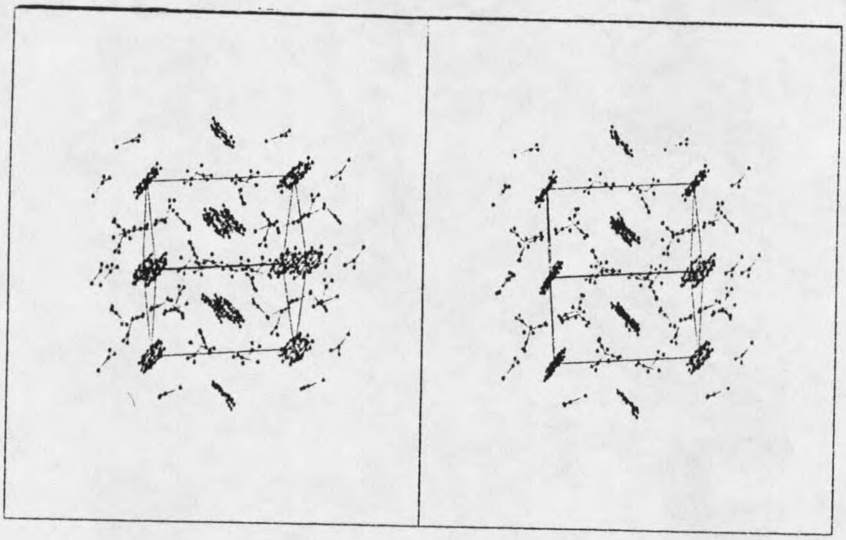


Figure 4. 1,2,4 TMB-thiourea complex viewed down the a-c diagonal.

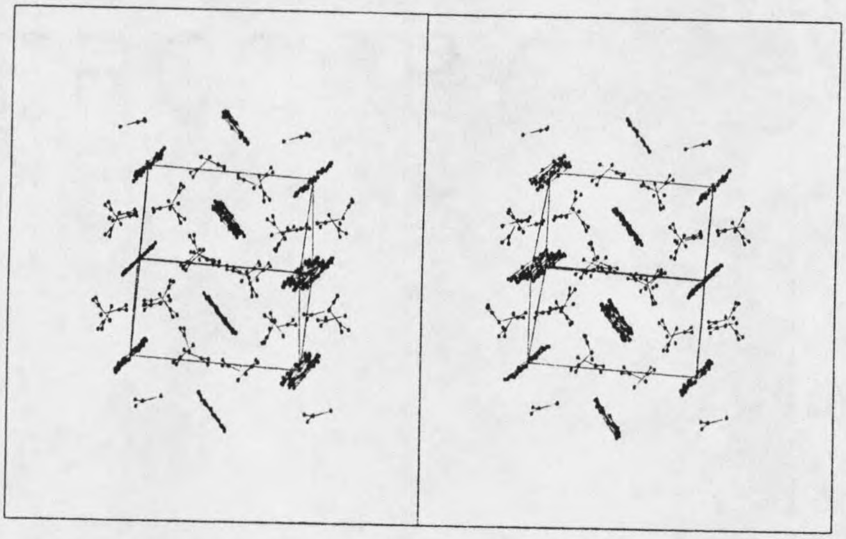


Figure 5. 1,2,4 TCB-thiourea complex viewed down the a-c diagonal.

center-to-center intermolecular distances and angles represented by this triangle are given in Table 9 for both complexes.

In order to obtain an idea of how the aromatic in the channel was situated a series of electron density difference maps were generated for the 1,2,4 TCB-thiourea adduct. The electron density difference map shown in Figure 11 was generated using only the refined thiourea. The view is looking down on the plane of the 1,2,4 trichlorobenzene. The contours range from -0.1 to 2.3 electrons per cubic angstrom.

Table 9. Center-to-center intermolecular bond distances and angles for the three coplaner sulfur atoms in the 1,2,4 TMB and 1,2,4 TCB adducts.

	1,2,4 TMB-Thiourea	1,2,4 TCB-Thiourea
	Distances A	
S1-S2	9.043	9.067
S2-S3	7.053	7.073
S3-S1	8.165	7.944
	Angles in Degrees	
<S1	48.1	48.6
<S2	59.4	57.4
<S3	72.5	74.0

The dotted lines are levels 0 and -0.1, the dashed lines are levels 0.1 to 1.1 and the solid lines are levels 1.1 to 2.3 electrons per cubic angstroms. The plot clearly shows the repeat down the channel of four peaks.

Upon superimposing an idealized 1,2,4 trichlorobenzene molecule in the channel it was evident that there are at least four different arrangements for which the molecule can satisfy the electron density

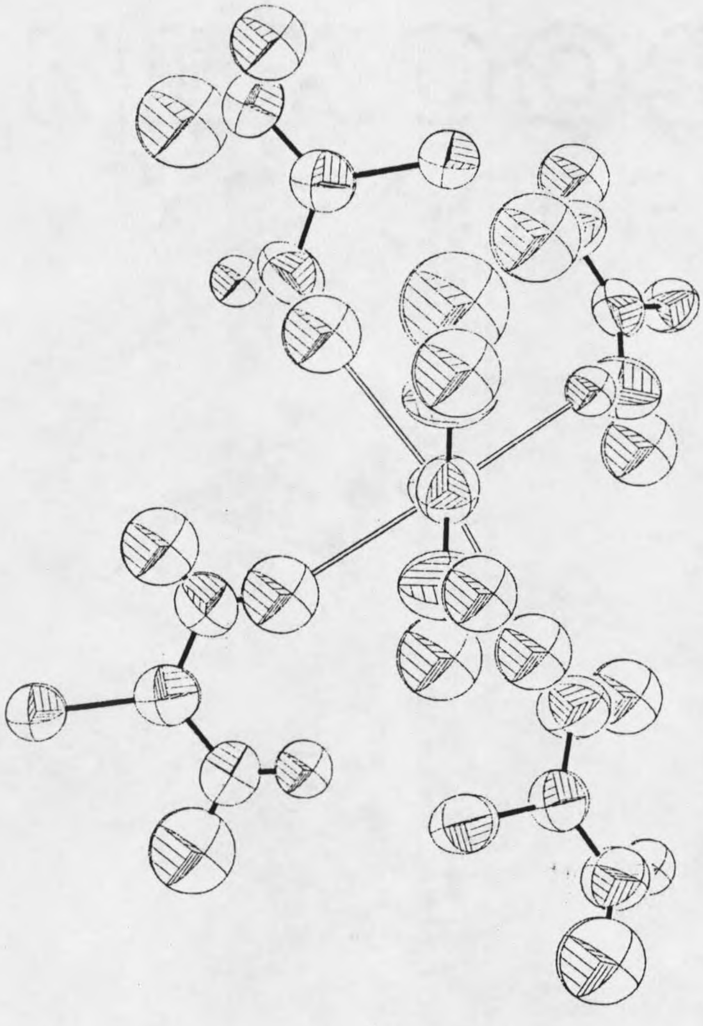


Figure 6. Hydrogen bonding scheme in the thiourea Lattice of the 1,2,4, TMB-thiourea adduct. The open lines are hydrogen bonds. The view is down the carbon=sulfur double bond.

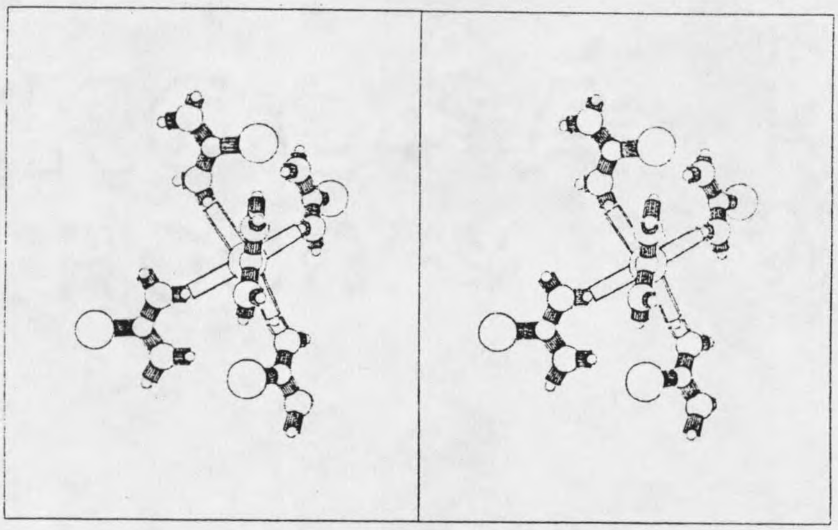


Figure 7. Steroview, down the carbon=sulfur double bond, of the hydrogen bonding network in within the thiourea lattice. Open lines are hydrogen bonds.

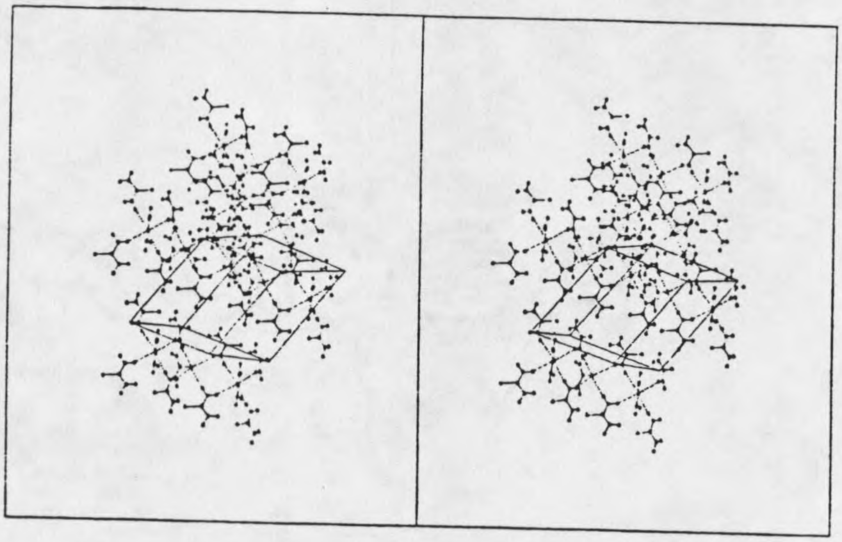


Figure 8. Steroview of the thiourea hydrogen bonding network, viewed down the a-c diagonal. Hydrogen bonds are drawn as dotted lines.

scheme. The combination of these arrangements yielded aromatic ring carbons overlapping chlorines and adjacent ring carbons. This gave an indication of the disorder which arose when constructing a model to describe the aromatic positioning in the channel. Figure 12 exhibits the electron density difference map with an idealized 1,2,4 trichlorobenze molecule superimposed in one of at least four possible arrangements.

Models for the aromatics in both complexes were constructed by constraining atoms in the channel which resembled a benzene ring and refining them using least squares. For the 1,2,4 TMB-thiourea complex this resulted in four benzene rings seen in Figure 13. The benzene rings are in pairs which are planer. The two planer pairs of rings are nearly in the same plane. The 1,2,4 TCB-thiourea complex yielded two benzene rings in the same plane. This model is shown in Figure 14. The open lines indicate that it is not known to which aromatic carbon the substituent is bond. In both models, atoms were added where peaks on the difference maps indicated a possible chlorine or methyl group.

Explanation of the disorder of the aromatics requires examination of the size and orientation of the guest and thiourea lattice. Within the thiourea lattice, coplaner sulfurs occur every third sulfur on the c-axis and this interplaner distance for both complexes is 12.54 A (Figure 2). The maximum lengths of a 1,2,4 trichlorobenzene molecule and of a 1,2,4 trimethybenzene molecule are 9.77 A and 9.25 A, respectively, including their van der Waal radii. Since the aromatics are found only within the region of the three coplaner sulfurs and

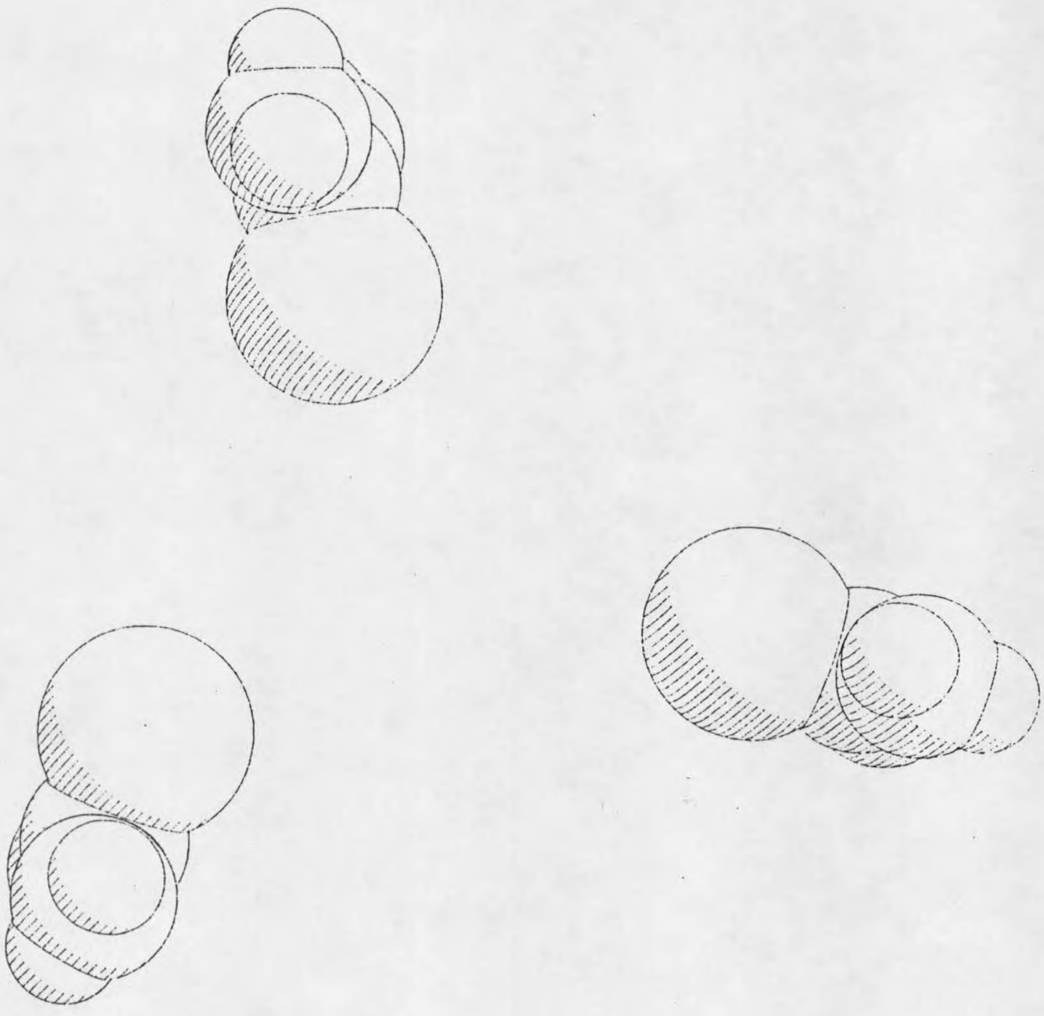


Figure 9. Space filling plot of the three coplaner suffer atoms of the 1,2,4, TCB-thiourea adduct pointing directly into the channel.

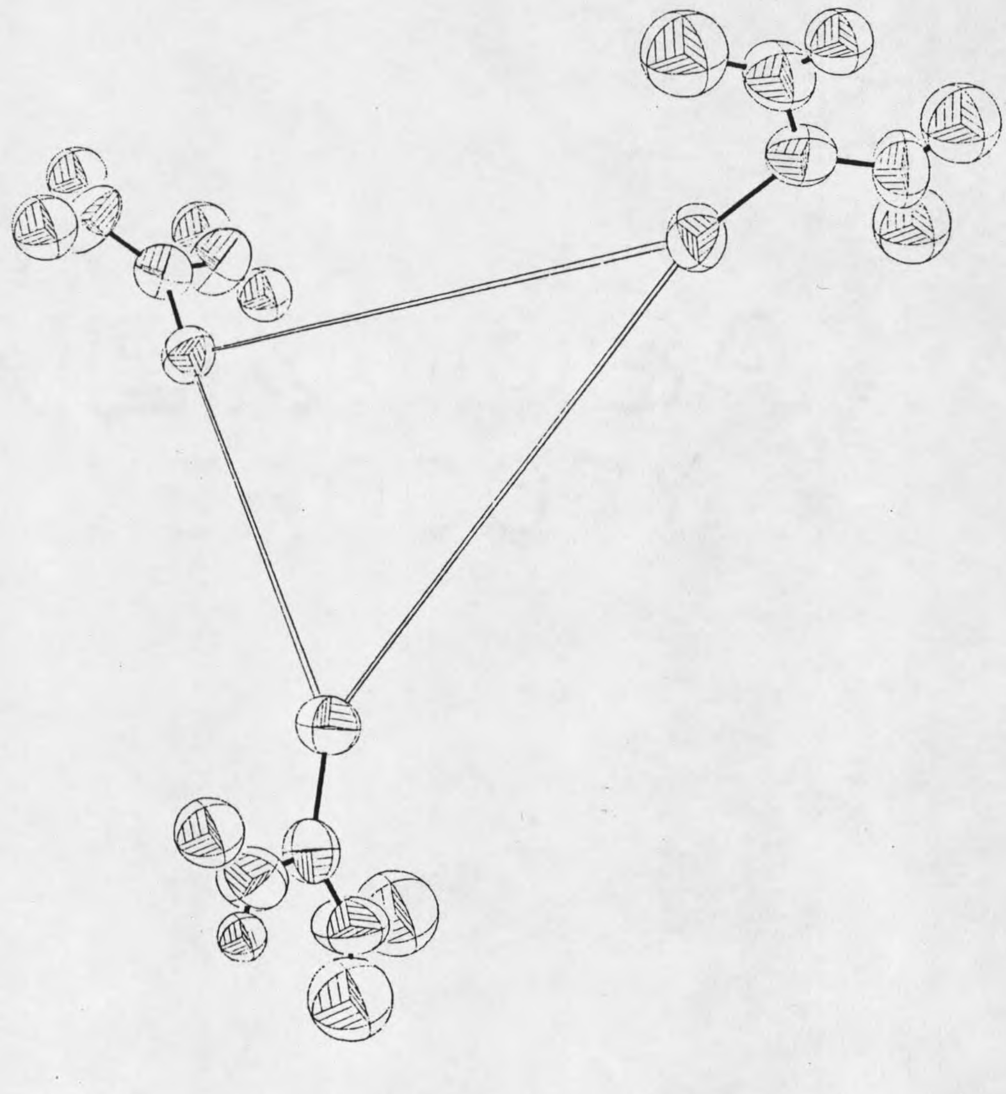


Figure 10. Three coplaner sulfur atoms of the 1,2,4 TCB-thiourea adduct with open lines defining the triangle formed by the sulfur atoms.

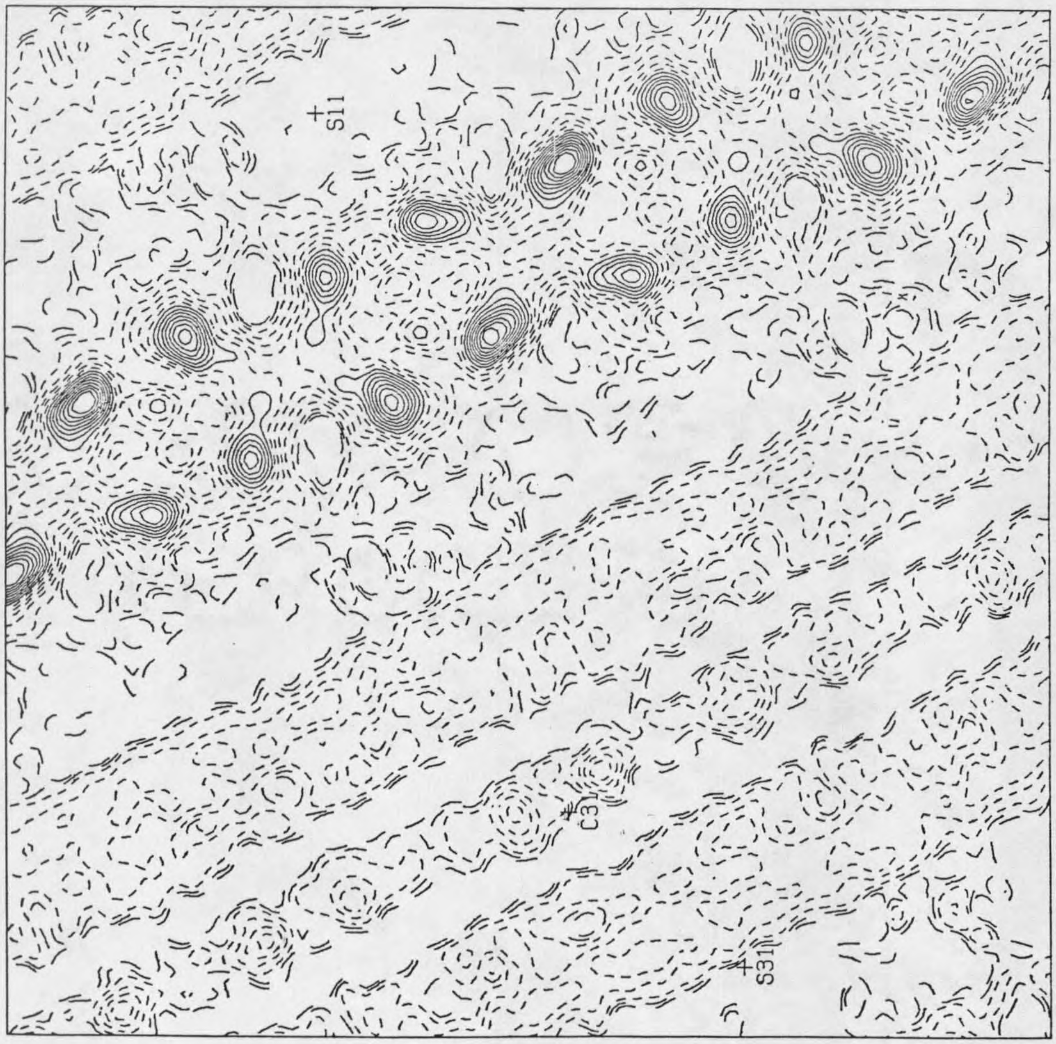


Figure 11. Electron density difference map of the 1,2,4 TCB-thiourea adduct. X = 24.107 A, Y = 24.107 A

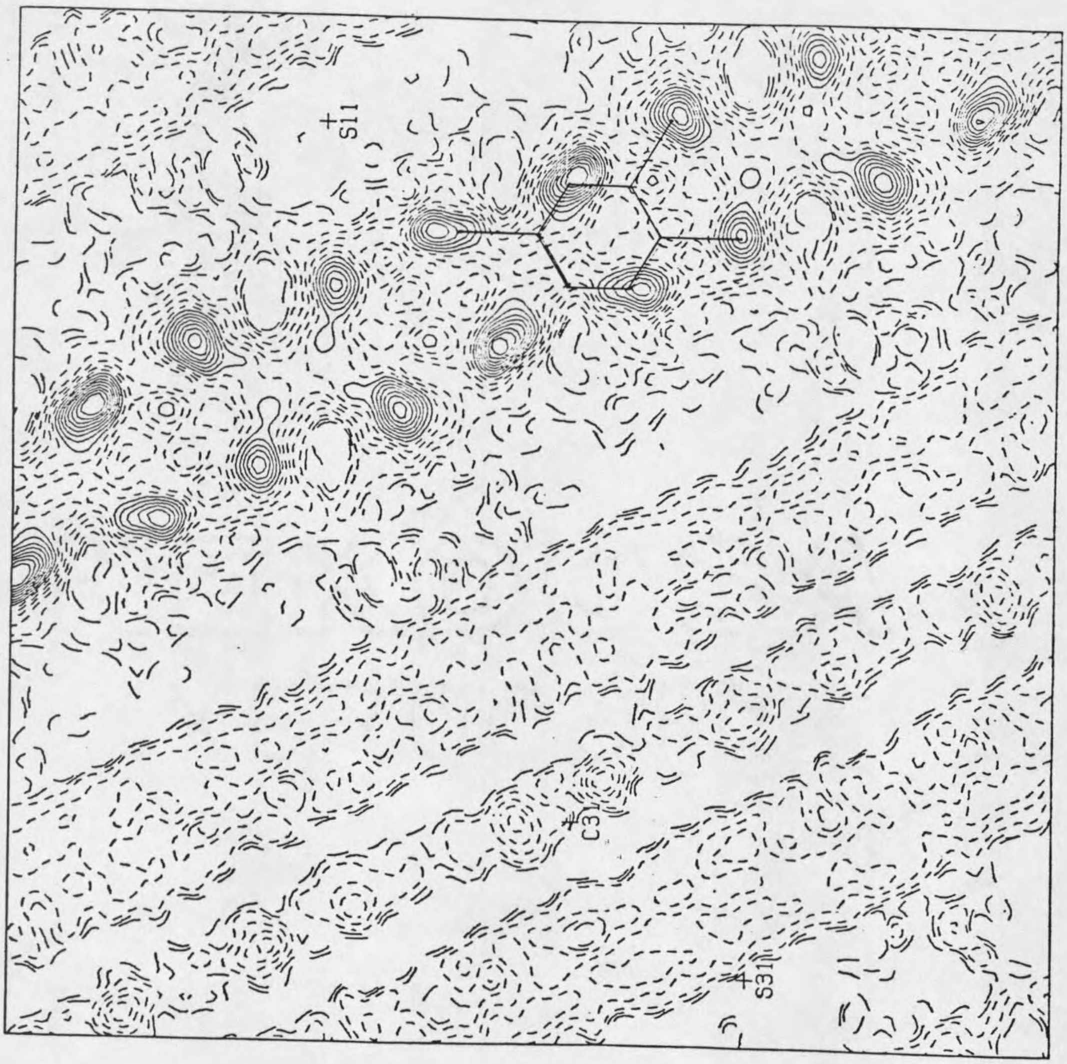


Figure 12. Electron density difference map of the 1,2,4 TCB-thiourea adduct with an idealized 1,2,4 TCB molecule superimposed. X = 24.107 A, Y = 24.107 A

their lengths are shorter than 12.54 A, disorder translationally seems to arise from site disorder and or orientation disorder and not adjacent aromatics overlapping into the next unit cell.

When the adducts are formed, the aromatics are equivalently positioned in the same channel unless there is a zone of maximum attraction unoccupied, then the preceeding aromatics may initiate another positioning along the channel which is different than that before the empty zone. Site disorder arises when the aromatics in a channel are positioned differently than aromatics in another channel. The disorder arises because the crystollographic data is an average of all the positions. If diffraction data could be obtained for each unit cell, the disorder could be resolved. The empty or unoccupied zones of maximum attraction are responsible for the non-stoichiometry of these complexes.

In the 1,2,4 TCB-thiourea complex and the 1,2,4 TMB-thiourea complex the aromatic ring might be positioned equally in any of two or more unit cells, however, the chlorines or methyl groups on the rings might be oriented differently. This is referred to as orientation disorder. This occurs since the aromatic ring can remain constant while the chlorines or methly groups are moved by rotating the aromatic 180°. It is site and or orientation disorder which are responsible for the 1,2,4 TCB and 1,2,4 TMB models having overlap of atoms.

The disordered aromatics prevent the precise location of the thiourea and aromatic interactions. Generally it can be said that the aromatic interacts with one or all of the three coplaner sulfurs. The

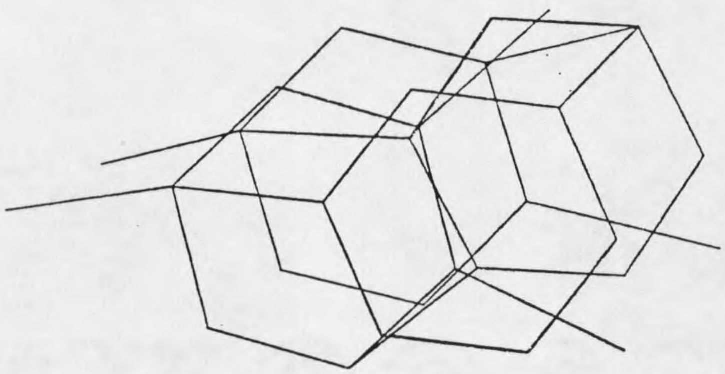


Figure 13. Model of the 1,2,4 TMB molecule in the 1,2,4, TMB-thiourea adduct.

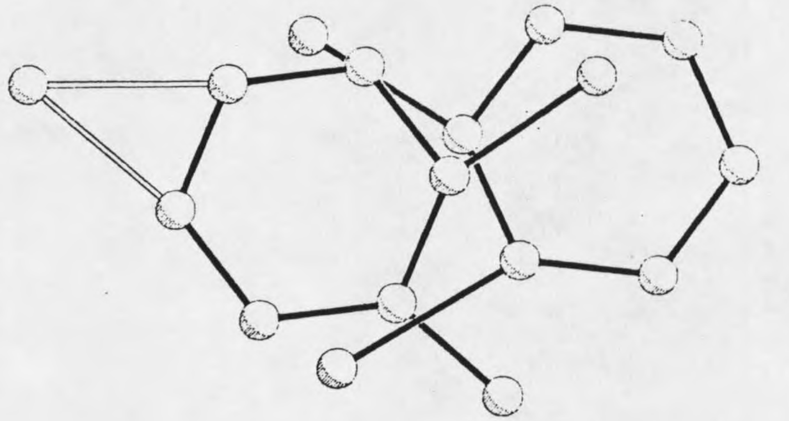


Figure 14. Model of the 1,2,4 TCB adduct in the 1,2,4 TCB-thiourea adduct. The open lines indicate that it is not known to which ring carbon the substituent is bonded.

nature of the strength of this interaction can be understood by studying the sulfur-carbon double bond length in the three coplaner sulfurs.

The sulfur-carbon double bond lengths in the three coplaner thiourea are 1.698(9) A, 1.706(10) A, 1.707(8) A, and 1.707(8) A, 1.698(9) A, 1.706(10) A for the 1,2,4, TCB adduct and the 1,2,4 TMB adduct respectively. These bond distances are about the same as the sulfur-carbon double bond distance found in pure thiourea. It can be concluded that the interaction between thiourea and the aromatic in an adduct is of the same magnitude as that of the hydrogen bonding in pure thiourea. Table 9 shows non-aromatic adducts having a stronger interaction due to the increased sulfur-carbon double band distances. This could account for the greater stability of non-aromatic adducts versus aromatic adducts.

A view of the 1,2,4, TCB model in the plane of the three coplaner sulfurs can be seen in Figure 15. The two non-solid bonds in the aromatic model indicate that it is not known which of the two aromatic carbons are bonded to the chlorine. Figure 15 and 16 show the relationship between the sulfur atoms and the aromatic. The three planer sulfur atoms can be seen pointing in at the 1,2,4 TCB model. Figure 16 is a view looking down the third thiourea's carbon-sulfur double bond. The angle of this figure shows that one sulfur is pointing directly into the middle of the planer rings while the other two are pointing into the sides of the rings. The non-bonded distances from each of these sulfur atoms to the rings are in Table 10.

The relationship between the coplaner sulfurs and the 1,2,4 TMB can be seen in Figures 17 through 20. Each of these figures exhibits only one of the four rings used in the model. If Figures 17 through 20 were superimposed, the result would be the four ring model positioned in the zone of the coplaner sulfurs. As in the 1,2,4, TCB-thiourea adduct, there is one sulfur pointing in at the plane of the 1,2,4 TMB model and the remaining two are pointing in at the sides. The non-bonded distances from each sulfur atom to the rings are listed in Table 11.

In both adducts, the distances from the sulfur pointing directly into the plane of the rings, and the aromatic carbons are all too long for a strong interaction to occur. The remaining two sulfurs oriented to the sides of the aromatic, are closer to some of the ring carbons. For a hydrogen bond to be possible, the atoms must be closer than the sum of their van der Waal radii and the carbon, hydrogen and sulfur must be linear. The van der Waal radius of sulfur is 1.76 and that for hyrogen is 1.20 A. The radius for a carbon-hydrogen covalent bond is 1.08 A. Thus, the shortest non-bonded distance between a linear carbon, hydrogen and sulfur is the sum of these radii, or 4.04 A. From Tables 10 and 11 only one sulfur-carbon nonbonded distance, S1A to B14 for the 1,2,4 TCB adduct and S1A to F4 for the 1,2,4 TMB adduct, are of the appropriate distance and angles necessary to be considered a hydrogen bond. Both these bonds are linear with a hydrogen in the middle and their distances are 4.001 A and 3.761 A for the 1,2,4 TCB adduct and 1,2,4 TMB adduct respectively. This indicates that a hydrogen bond is a possibility.

Table 10. Interatomic distances between sulfur and carbon in the 1,2,4 TCB-thiourea adduct structure. Only distances less than about 4.5 A are tabulated.

Atom 1	Atom 2	Distance in A
S1A	B1	3.991
S1A	B2	4.485
S1A	B14	4.001
S2A	B11	4.111
S2A	B12	3.709
S2A	B13	4.026
S2A	B1	4.439
S2A	B4	4.108
S2A	B5	3.713
S2A	B6	3.899
S3A	B11	4.355
S3A	B12	4.243
S3A	B4	4.550
S3A	B5	4.078

The other most likely form of interaction is a dipole-dipole attraction between the sulfurs and the aromatic carbons. This would require the two unshaired pairs of electrons on the sulfurs inducing an added dipole in the aromatic C-H group. Whether the interaction between the thiourea and the aromatic is of a hydrogen bonding type and, or a dipole-dipole type the interaction does contribute to lowering the energy state of the complex.

The possibility of hydrogen bonding and the evidence of dipole-dipole interations might contribute to the predicting of which hydrocarbon will or will not adduct.

Table 11. Interatomic distances between sulfur and carbon in the 1,2,4 TMB-thiourea adduct structure. Only distances less than about 4.5A are tabulated.

Atom 1	Atom 2	Distance in A
S1A	B4	4.234
S1A	F3	4.539
S1A	F4	3.761
S1A	B25	4.424
S1A	B26	4.483
S2A	B1	3.925
S2A	B6	3.784
S2A	T3	3.724
S2A	T1	3.965
S2A	T2	3.744
S2A	F1	3.569
S2A	F2	4.066
S2A	F6	3.825
S2A	B21	3.763
S2A	B22	3.735
S3A	B1	3.875
S3A	B6	4.116
S3A	T3	4.127
S3A	T1	3.894
S3A	T2	3.410
S3A	F1	3.950
S3A	F2	4.440
S3A	F6	4.584
S3A	B21	4.396
S3A	B22	3.823

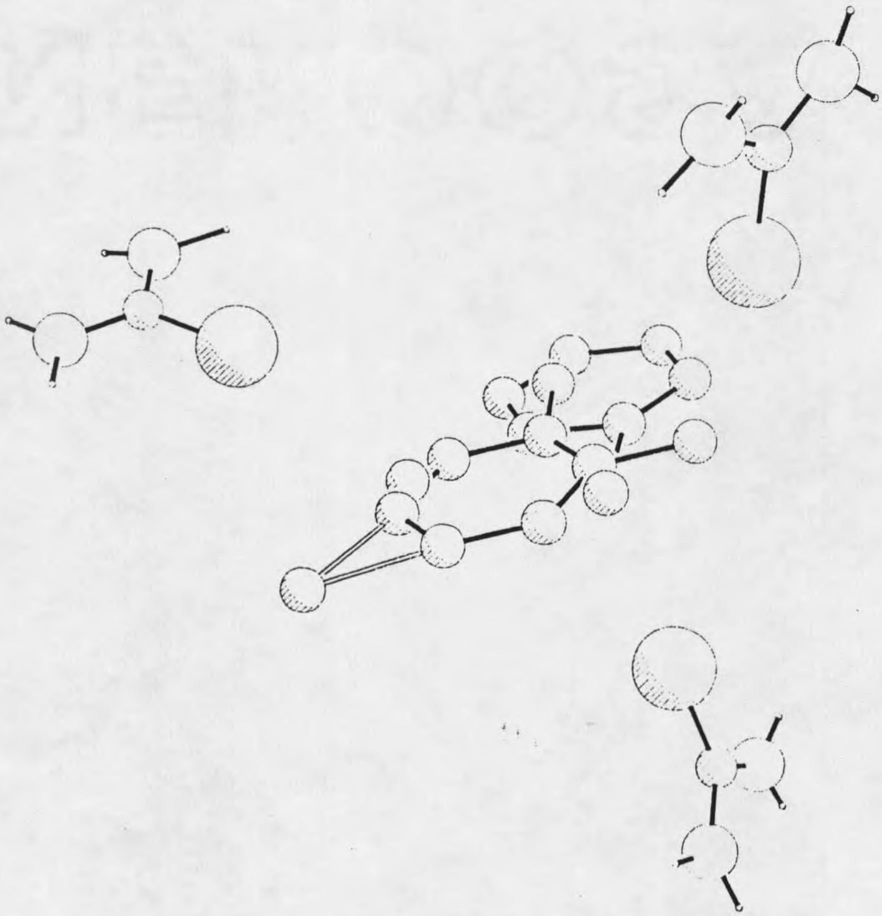


Figure 15. View of the 1,2,4 TCB model in the region of the three coplaner sulfurs.

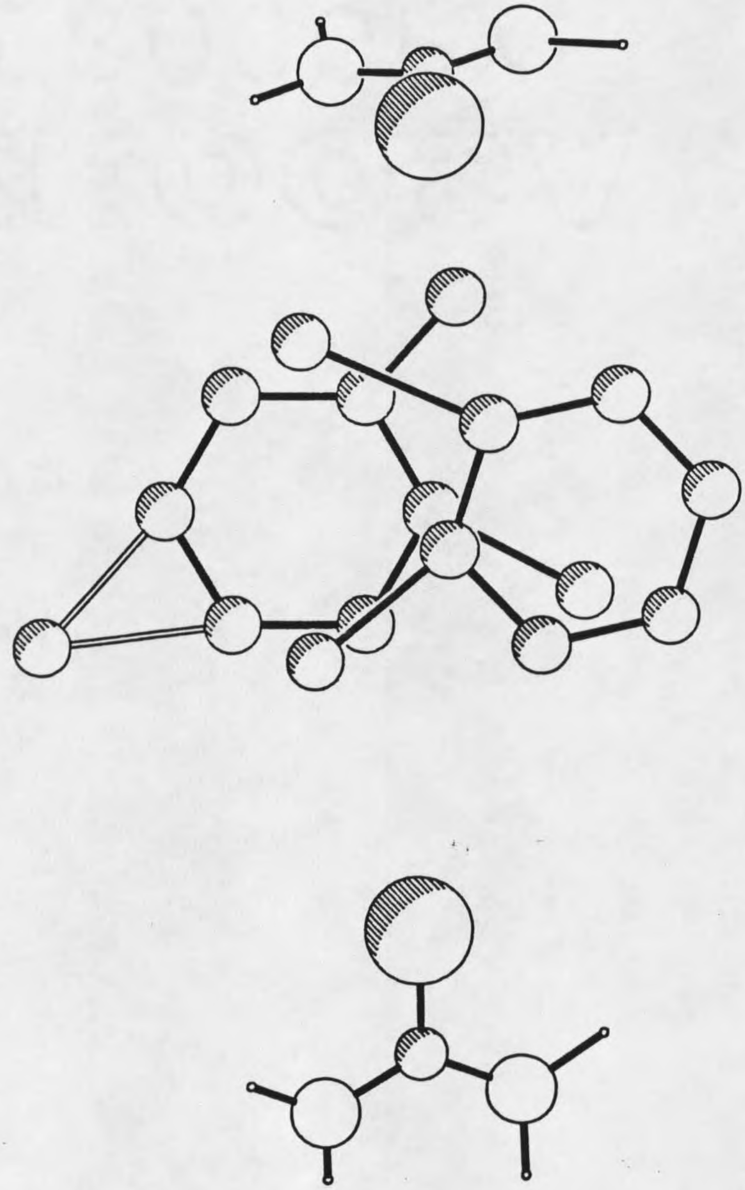


Figure 16. Two thiourea molecules with planer sulfur atoms pointing into the sides of the 1,2,4 TCB model view in looking down the sulfur=carbon double bond of the third coplaner sulfur.

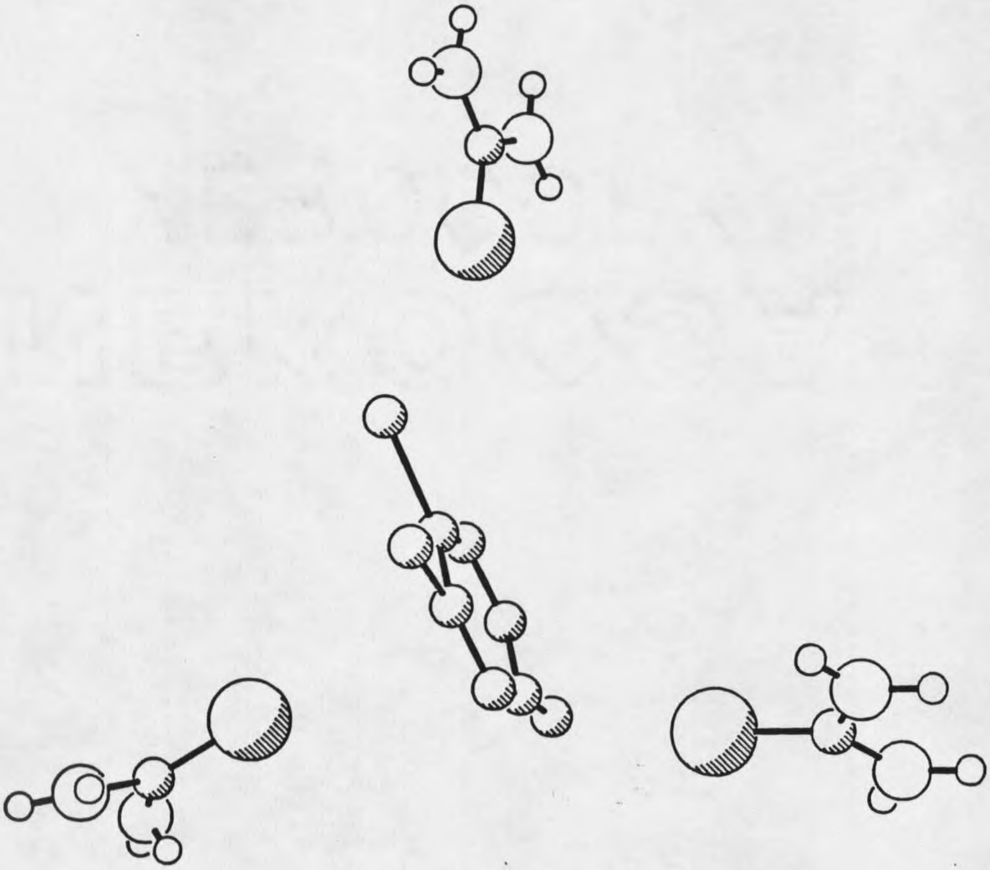


Figure 17. One of the four model rings of the 1,2,4, TMB shown in the region of the three coplaner sulfurs.

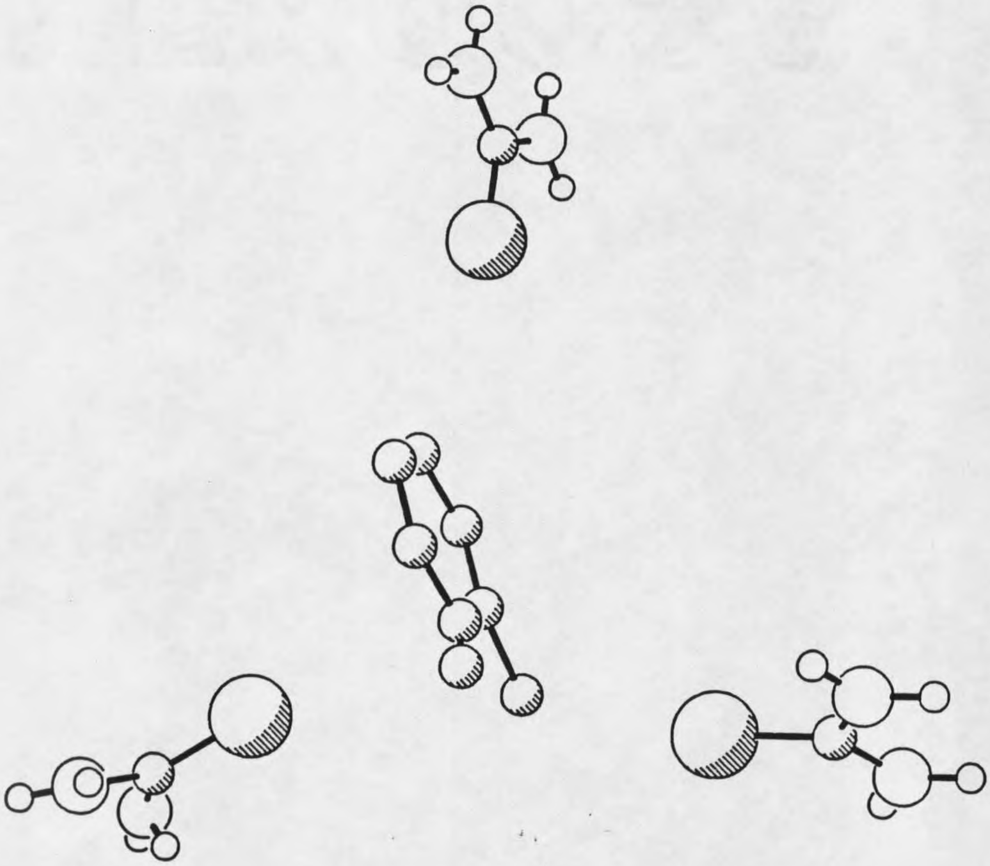


Figure 18. One of the four model rings of the 1,2,4 TMB shown in the region of the three coplaner sulfurs.

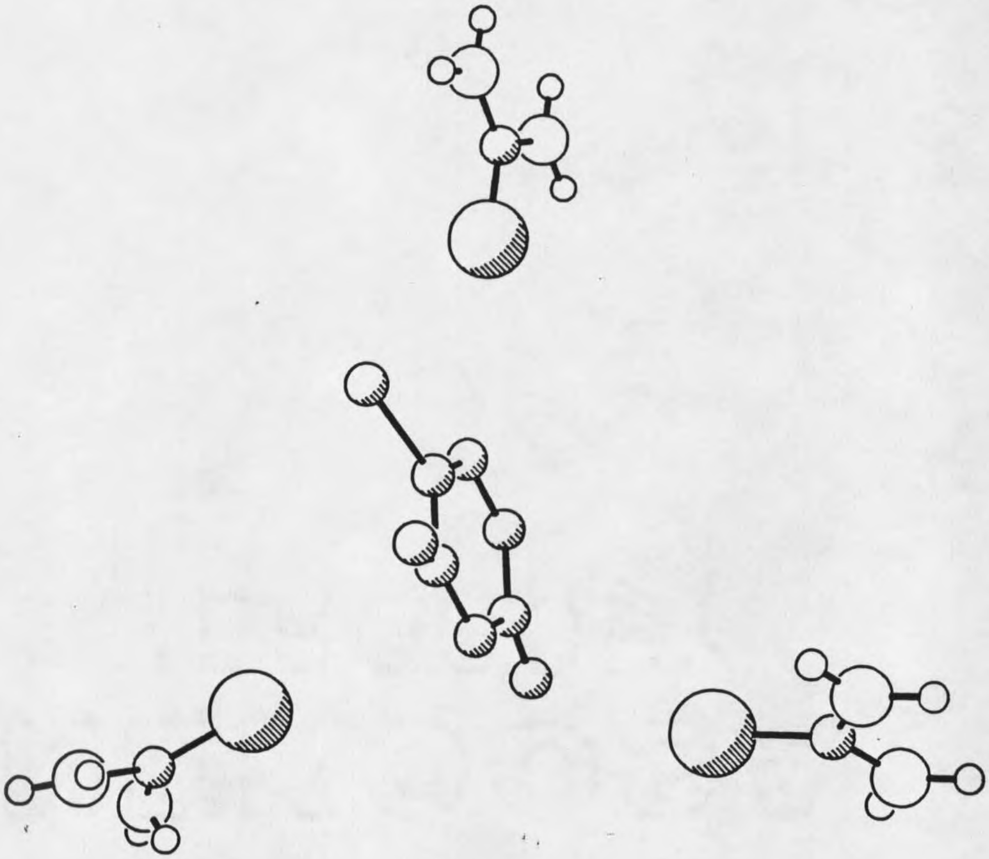


Figure 19. One of the four model rings of the 1,2,4 TMB shown in the region of the three coplaner sulfurs.

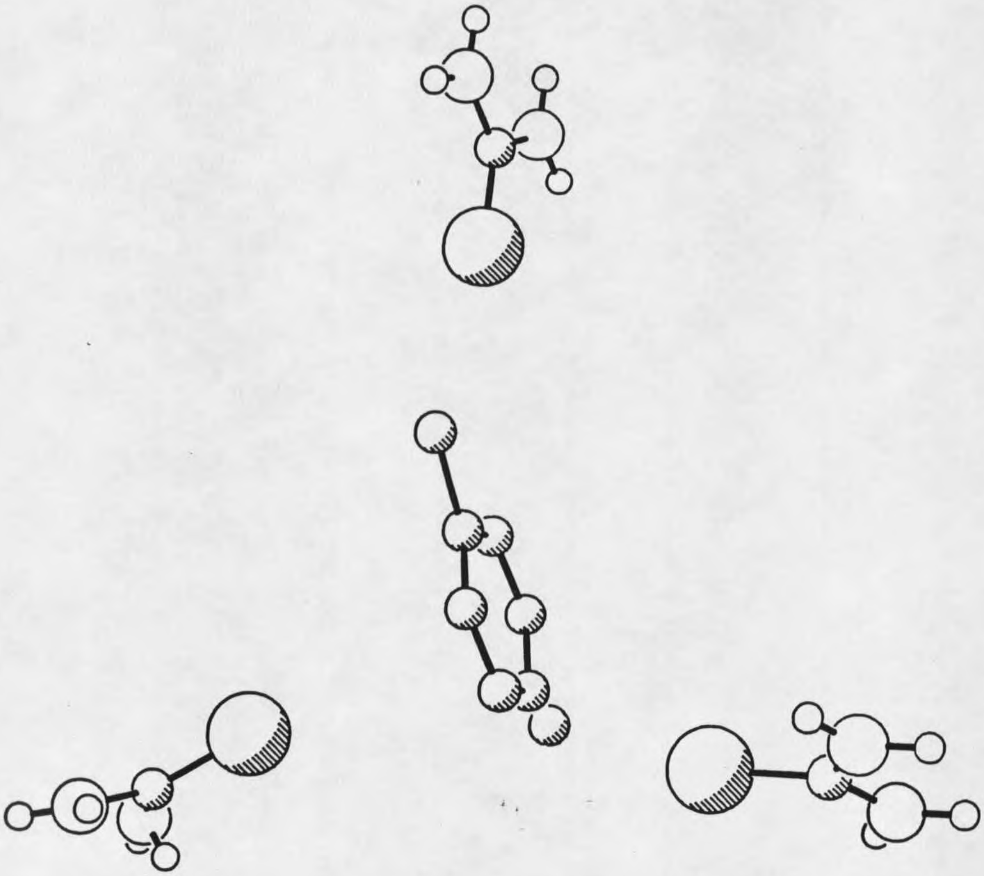


Figure 20. One of the four model rings of the 1,2,4 TMB shown in the region of the three coplaner sulfurs.

CONCLUSIONS

Extractive crystallization with thiourea is a novel separations technique which separates hydrocarbons and notably aromatic systems. In the extractive crystallization process, a unique crystalline complex is formed when thiourea spirals around a selected hydrocarbon and forms a cage-like entrapment. Thiourea is selective for classes of hydrocarbons and is even selective between isomers of the same emperical formula. The entrapped hydrocarbon can be recovered from the complex by steam stripping, followed by phase separation of the products.

Knowledge of the atomic positions, intermolecular distances and the intermolecular forces of interaction in these thiourea complexes might allow an understanding of their selectivity and stability. From x-ray crystallographic data the thiourea lattice is well defined in these complexes. Schlenk discovered the zones of maximum attraction occurring in each unit cell where three coplaner sulfur atoms are pointing directly into the channel. The thiourea molecules are bonded to one another via hydrogen bonds. This accounts for a part of the stability, but not the selectivity of these thiourea adducts. The key to the selectivity of these complexes is thought to lie in the thiourea/hydrocarbon interaction.

Supporting evidence for an interaction lies in the fact that thiourea will form adducts with some compounds yet not with other compounds of similar size and shape. In addition, the carbon-sulfur double bond distance in thiourea varies between aromatic and non-aromatic complexes. This is an indication that there is an interaction and that it is flexible in nature. Finally, the nonbonded distances between the coplaner sulfurs and the aromatic are almost at the distance equal to the sum of the van der Waal radii and, in each adduct one nonbonded distance is within the appropriate length and geometry to indicate a possible hydrogen bond. The nonbonded distances close to the van der Waal radii of the aromatic indicate a dipole-dipole interaction.

If in fact a hydrogen bond does exist some credibility might be added to Fetterly's notion of a "supported hydrogen bond". However, the probability of dipole-dipole attractions occurring should not be ruled out. Fetterly's idea does not explain explain adducts which have no possibilities of hydrogen bonding, i.e. carbon tetrachloride adduct. No evidence was found to support Welling's suggestion of a chlorine/NH_2 group hydrogen bond in the 1,2,4 TCB thiourea adduct. Furthermore, no hydrogen bonding was seen between a methyl group and a sulfur in the 1,2,4 TMB-thiourea adduct.

Diffractometer data sets collected on both the 1,2,4 TMB-thiourea and 1,2,4 TCB-thiourea adducts showed both adducts crystallizing in the space group P21/c, which is characteristic of aromatic complexes. The most difficult problem associated with both complexes was the disorder of the aromatic in the channel. The disorder arose from site and or orientation disorder and not adjacent aromatics overlapping each other. A model which take into account the disorder was found for each complex. Refinement of these models resulted in an R value of .1053 for the 1,2,4 TBM adduct and .0951 for the 1,2,4 TCB adduct. Both aromatic models where found to lie in the zone of maximum attraction created by the three coplaner sulfur atoms in the thiourea lattice. It is hoped that the information concerning the structures of these adduct can be used in future research to determine the overall selectivity mechanism of these thiourea adducts.

Recommendations

Many aromatic and non-aromatic hydrocarbons form adducts with thiourea. The wide range of stability and selectivity of these adducts pose many questions regarding their structures and chemical interactions. The knowledge of the exact nature of the thiourea and hydrocarbon interaction appears to be vital if the selectivity mechanism and chemical structures are to be known. The primary obstacle is resolving the disorder associated with the channel hydrocarbon.

Steps taken to reduce the disorder might entail utilizing a guest hydrocarbon, such as carbon tetrabromide, which possesses heavy atoms that could appear less disordered in the difference maps. Alternatively, a better 1,2,4 TCB model refined using a full matrix least squares in the XTAL system might enhance locating the chlorine atoms in the 1,2,4 TCB adduct. Another approach might be to find a guest hydrocarbon which is geometrically large enough so that the number of orientations possible in the channel are minimized, thus reducing the orientation disorder. Furthurmore, if a larger guest hydrocarbon could be found that occupied two or more zones of maximum attraction the site disorder might be reduced. The quality of the x-ray diffraction data could be enhanced if data set were obtained using low temperatures.

Although 1,2,4 trichlorobenzene is considered to be an inductor, the role of inductors in thiourea complexes was not fully investigated in the two aromatic adducts studied. It appears that the role of an inductor must be studied in adducts which contain the inductor and selected hydrocarbon. For instance, CCl_4 is selective for ethylbenzene in the aromatic mixture of ethylbenzene and oxylene. In the same mixture, 1,2,4 trichlorobenzene is selective for the o-xylene. Since CCl_4 adducts in space group R3bar and 1,2,4, TCB adducts in P21/c it would be interesting to see which space group forms when CCl_4 inducts ethylbenzene and when 1,2,4 TCB inducts o-xylene.

The same intermolecular forces which appear in the crystalline adduct are also present in solution. Therefore, nuclear magnetic resonance (nmr) spectroscopy and infared spectroscopy may shed light on the intermolecular interaction between the thiourea and the hydrocarbon.

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LITERATURE CITED

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APPENDICES

APPENDIX A

CLASSIFICATION OF CRYSTALS

APPENDIX A

There are seven three-dimentional coordinate systems which are used to classify crystals (18). In general, the unit cell is characterized by a certain symmetry and six parameters, three axial lengths and three interaxial angles. The lengths of the unit cell edges are designated a, b, c and the interaxial angles α, β, γ where is the angle between b and c, β is the angle between a and c, and γ is between a and b.

The following table specifies the seven crystal systems along with the corresponding unit cell parameters:

Table 12. The seven possible crystal systems.

Crystal System	No. Independent Parameters	Parameters	Lattice Symmetry
Triclinic	6	$a \neq b \neq c$; $\alpha \neq \beta \neq \gamma$	1
Monoclinic	4	$a \neq b \neq c$; $\alpha = \gamma = 90°$; $\beta \neq 90°$	2/m
Orthorhombic	3	$a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$	mmm
Tetragonal	2	$a = b \neq c$; $\alpha = \beta = \gamma = 90°$	4/mmm
Rhombohedral	2	$a = b = c$; $\alpha = \beta = \gamma \neq 90°$	3/m
Hexagonal	2	$a = b \neq c$; $\alpha = \beta = 90°$; $\gamma = 120°$	6/mmm
Cubic	1	$a = b = c$; $\alpha = \beta = \gamma = 90°$	m3m

The essential symmetries of a structure can be categorized into systems referred to as the Laue Space Groups. There are 230 space groups, each unique in describing a particular crystal's internal (i.e. molecular) symmetry. A crystal's space group can be determined by systematic x-ray reflection absences, and the space group is listed in the "International Tables for X-Ray Crystallography." All symmetry elements are represented by symbols, figures and letters which are arranged together to indicate a space group.

Table 13. Symbols for symmetry elements and for the corresponding symmetry operations in one-, two-, and three-dimensions [reproduced from (8)].

Printed symbol	Symmetry element and its orientation	Generating symmetry operation with glide or screw vector
	Reflection plane, mirror plane	Reflection through a plane
m	Reflection line, mirror line (two dimensions)	Reflection through a line
	Reflection point, mirror point (one dimension)	Reflection through a point
a, b, or c	'Axial' glide plane	Glide reflection through a plane, with glide vector
a	$\perp[010]$ or $\perp[001]$	$\frac{1}{2}\mathbf{a}$
b	$\perp[001]$ or $\perp[100]$	$\frac{1}{2}\mathbf{b}$
	$\perp[100]$ or $\perp[010]$	$\frac{1}{2}\mathbf{c}$
c	$\perp[1\bar{1}0]$ or $\perp[110]$	$\frac{1}{2}\mathbf{c}$
	$\perp[100]$ or $\perp[010]$ or $\perp[\bar{1}\bar{1}0]$	$\frac{1}{2}\mathbf{c}$ hexagonal coordinate system
	$\perp[1\bar{1}0]$ or $\perp[120]$ or $\perp[\bar{2}\bar{1}0]$	$\frac{1}{2}\mathbf{c}$ hexagonal coordinate system
n	'Diagonal' glide plane	Glide reflection through a plane, with glide vector
	$\perp[001]$; $\perp[100]$; $\perp[010]$	$\frac{1}{2}(\mathbf{a}+\mathbf{b})$; $\frac{1}{2}(\mathbf{b}+\mathbf{c})$; $\frac{1}{2}(\mathbf{a}+\mathbf{c})$
	$\perp[1\bar{1}0]$ or $\perp[01\bar{1}]$ or $\perp[\bar{1}01]$	$\frac{1}{2}(\mathbf{a}+\mathbf{b}+\mathbf{c})$
	$\perp[110]$; $\perp[011]$; $\perp[101]$	$\frac{1}{2}(-\mathbf{a}+\mathbf{b}+\mathbf{c})$; $\frac{1}{2}(\mathbf{a}-\mathbf{b}+\mathbf{c})$; $\frac{1}{2}(\mathbf{a}+\mathbf{b}-\mathbf{c})$
d	'Diamond' glide plane	Glide reflection through a plane, with glide vector
	$\perp[001]$; $\perp[100]$; $\perp[010]$	$\frac{1}{4}(\mathbf{a}\pm\mathbf{b})$; $\frac{1}{4}(\mathbf{b}\pm\mathbf{c})$; $\frac{1}{4}(\pm\mathbf{a}+\mathbf{c})$
	$\perp[1\bar{1}0]$; $\perp[01\bar{1}]$; $\perp[\bar{1}01]$	$\frac{1}{4}(\mathbf{a}+\mathbf{b}\pm\mathbf{c})$; $\frac{1}{4}(\pm\mathbf{a}+\mathbf{b}+\mathbf{c})$; $\frac{1}{4}(\mathbf{a}\pm\mathbf{b}+\mathbf{c})$
	$\perp[110]$; $\perp[011]$; $\perp[101]$	$\frac{1}{4}(-\mathbf{a}+\mathbf{b}\pm\mathbf{c})$; $\frac{1}{4}(\pm\mathbf{a}-\mathbf{b}+\mathbf{c})$; $\frac{1}{4}(\mathbf{a}\pm\mathbf{b}-\mathbf{c})$
g	Glide line (two dimensions)	Glide reflection through a line, with glide vector
	$\perp[01]$; $\perp[10]$	$\frac{1}{2}\mathbf{a}$; $\frac{1}{2}\mathbf{b}$
1	None	Identity
2,3,4,6	n-fold rotation axis, n	Counter-clockwise rotation of $360/n$ degrees around an axis
	n-fold rotation point, n (two dimensions)	Counter-clockwise rotation of $360/n$ degrees around a point
$\bar{1}$	Centre of symmetry, inversion centre	Inversion through a point
$\bar{2}=m$, $\bar{3},\bar{4},\bar{6}$	Rotoinversion axis, $\bar{n}$	Counter-clockwise rotation of $360/n$ degrees around an axis, followed by inversion through a point on the axis
2_1 $3_1, 3_2$ $4_1, 4_2, 4_3$ $6_1, 6_2, 6_3, 6_4, 6_5$	n-fold screw axis, n_p	Right-handed screw rotation of $360/n$ degrees around an axis, with screw vector (pitch) $(p/n)\,\mathbf{t}$; here $\mathbf{t}$ is the shortest lattice translation vector parallel to the axis in the direction of the screw

Table 14. Symbols for one-, two-, and three-dimensional cells [reproduced from (8)].

Printed symbol	Centring type of cell	Number of lattice points per cell	Coordinates of lattice points within cell
One dimension			
𝓅	Primitive	1	0
Two dimensions			
p	Primitive	1	0,0
c	Centred	2	0,0; $\frac{1}{2},\frac{1}{2}$
h	Hexagonally centred	3	0,0; $\frac{2}{3},\frac{1}{3}$; $\frac{1}{3},\frac{2}{3}$
Three dimensions			
P	Primitive	1	0,0,0
C	*C*-face centred	2	0,0,0; $\frac{1}{2},\frac{1}{2}$,0
A	*A*-face centred	2	0,0,0; 0,$\frac{1}{2},\frac{1}{2}$
B	*B*-face centred	2	0,0,0; $\frac{1}{2}$,0,$\frac{1}{2}$
I	Body centred	2	0,0,0; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$
F	All-face centred	4	0,0,0; $\frac{1}{2},\frac{1}{2}$,0; 0,$\frac{1}{2},\frac{1}{2}$; $\frac{1}{2}$,0,$\frac{1}{2}$
R	Rhombohedrally centred (description with 'hexagonal axes')	3	0,0,0; $\frac{2}{3},\frac{1}{3},\frac{1}{3}$; $\frac{1}{3},\frac{2}{3},\frac{2}{3}$ ('obverse setting') 0,0,0; $\frac{1}{3},\frac{2}{3},\frac{1}{3}$; $\frac{2}{3},\frac{1}{3},\frac{2}{3}$ ('reverse setting')
	Primitive (description with 'rhombohedral axes')	1	0,0,0
H	Hexagonally centred	3	0,0,0; $\frac{2}{3},\frac{1}{3}$,0; $\frac{1}{3},\frac{2}{3}$,0

APPENDIX B

ELEMENTAL ANALYSIS

APPENDIX B

Table 15. Elemental analysis for the 1,2,4 TCB-thiourea adduct, the 1,2,4 TMB-thiourea adduct, and pure thiourea.

(I) 1,2,4 TCB-Thiourea Adduct

Sample Weight (mg)	Nitrogen %	Carbon %	Hydrogen %
1.2829	22.00	24.68	3.83
1.1389	22.46	24.35	3.85
1.8014	21.61	24.66	3.84

(II) 1,2,4 TMB-Thiourea Adduct

Sample Weight (mg)	Nitrogen %	Carbon %	Hydrogen %
1.4673	26.93	35.58	6.68
1.5272	27.07	35.40	6.68
1.4972	25.77	37.04	6.81

(III) Pure Thiourea

% C	% H	% N	% S	% O
15.83	5.29	37.18	41.65	0.06

APPENDIX C

TABLES FOR PUBLICATION FOR THE
1,2,4 TCB-THIOUREA ADDUCT STRUCTURE

APPENDIX C

Table 16. Atomic coordinates and isotropic thermal parameters for the 1,2,4 TCB-thiourea adduct structure.

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\AA^2 \times 10^3$)

	x	y	z	U
B(5)	3317(28)	10410(13)	2589(15)	211(10)
B(6)	2143	9865	2511	362
B(1)	2198	9366	3475	374(17)
B(2)	3427	9413	4518	184(7)
B(3)	4601	9958	4596	264(19)
B(4)	4546	10457	3632	131(8)
B(11)	1635(21)	10462(11)	667(15)	186(8)
B(12)	2507	10258	1824	513(46)
B(13)	1982	9687	2461	687(49)
B(14)	584	9318	1940	139(4)
B(15)	-288	9522	783	356(43)
B(16)	237	10094	146	746
S(1)	3975(2)	6472(1)	4397(2)	73(1)*
S(2)	-88(2)	6370(1)	1410(2)	67(1)*
S(3)	3182(2)	3030(1)	2024(2)	70(1)*
C(1)	2765(9)	6881(5)	4970(7)	69(4)*
C(2)	899(8)	7081(5)	936(7)	66(3)*
C(3)	2719(7)	4073(5)	2226(6)	66(3)*
N(11)	1337(6)	6951(5)	4296(5)	82(3)*
N(12)	3228(7)	7157(4)	6067(5)	89(3)*
N(21)	2294(9)	7263(6)	1570(8)	91(4)*
N(22)	268(11)	7465(6)	-88(8)	88(4)*
N(31)	1774(7)	4529(4)	1362(5)	91(3)*
N(32)	3271(10)	4437(6)	3285(7)	95(4)*
Cl(1)	4042(65)	11046(40)	2154(54)	423(34)
Cl(2)	4819(27)	9341(16)	6008(20)	122(8)
Cl(3)	482(59)	9615(29)	1213(39)	235(20)
Cl(5)	4425(14)	10714(8)	3105(11)	55(3)
Cl(6)	2411(20)	10740(12)	867(15)	85(5)
Cl(7)	2848(29)	10757(20)	1335(25)	116(11)
Cl(4)	2515(23)	9275(14)	3948(19)	94(6)

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 17. Anisotropic thermal parameters for the 1,2,4 TCB-thiourea adduct structure.

Anisotropic thermal parameters ($\AA^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	61(1)	90(1)	64(1)	-13(1)	17(1)	3(1)
S(2)	60(1)	73(1)	62(1)	9(1)	18(1)	-2(1)
S(3)	81(1)	69(1)	54(1)	-2(1)	18(1)	12(1)
C(1)	71(6)	69(6)	65(5)	3(5)	24(5)	-8(5)
C(2)	67(5)	70(6)	63(5)	-4(4)	26(4)	7(4)
C(3)	65(4)	65(5)	68(4)	-6(4)	24(4)	-4(4)
N(11)	56(3)	107(5)	83(4)	3(4)	24(3)	2(4)
N(12)	78(4)	120(6)	70(4)	-24(4)	30(3)	1(4)
N(21)	63(5)	116(7)	89(6)	7(5)	23(5)	-21(5)
N(22)	116(7)	87(7)	70(5)	17(4)	43(5)	-11(5)
N(31)	98(5)	72(4)	77(4)	3(4)	4(4)	13(4)
N(32)	120(7)	65(5)	82(5)	-9(5)	15(5)	7(5)

The anisotropic temperature factor exponent takes the form:

$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$

Table 18. H-atom coordinates and isotropic thermal parameters for the 1,2,4 TCB-thiourea adduct structure.

H-Atom coordinates ($\times 10^4$) and isotropic thermal parameters ($\AA^2 \times 10^3$)

	x	y	z	U
H(12a)	2541	7399	6375	105
H(12b)	4252	7111	6557	105
H(1)	635(66)	7443(39)	4594(52)	83(19)
H(2)	600(133)	6539(80)	2967(109)	255(50)
H(21)	2889(81)	7142(52)	2386(67)	144(29)
H(22)	2875(104)	7473(65)	1416(85)	115(40)
H(23)	615(69)	7640(43)	-258(58)	6(19)
H(24)	-530(132)	7252(79)	-1218(114)	269(53)
H(31)	3753(78)	4065(48)	3801(60)	84(26)
H(32)	3319(65)	4929(37)	3279(51)	36(19)
H(33)	1653(92)	5087(65)	1248(81)	181(38)
H(34)	1354(75)	4214(47)	629(62)	106(24)

Table 19. Bond lengths for the 1,2,4 TCB-thiourea adduct structure.

Bond lengths (Å)

S(1)-C(1)	1.706(10)	S(2)-C(2)	1.698(9)
S(2)-H(2)	1.796(124)	S(3)-C(3)	1.707(8)
C(1)-N(11)	1.337(9)	C(1)-N(12)	1.322(10)
C(2)-N(21)	1.325(10)	C(2)-N(22)	1.318(11)
C(3)-N(31)	1.320(8)	C(3)-N(32)	1.332(10)
N(11)-H(1)	1.168(69)	N(21)-H(21)	0.973(69)
N(21)-H(22)	0.736(113)	N(22)-H(23)	0.532(77)
N(22)-H(24)	1.356(125)	N(31)-H(33)	0.869(101)
N(31)-H(34)	0.969(72)	N(32)-H(31)	0.853(66)
N(32)-H(32)	0.757(58)	Cl(1)-B(5)	1.423(73)
Cl(1)-B(4)	1.922(66)	Cl(1)-B(12)	1.851(64)
Cl(1)-Cl(5)	1.200(64)	Cl(1)-Cl(6)	1.841(53)
Cl(1)-Cl(7)	1.303(57)	Cl(2)-B(2)	1.834(26)
Cl(2)-B(3)	1.918(32)	Cl(2)-B(3a)	1.530(36)
Cl(2)-B(4a)	0.687(31)	Cl(2)-Cl(5a)	1.069(24)
Cl(3)-B(6)	1.844(47)	Cl(3)-B(11)	1.993(60)
Cl(3)-B(13)	1.685(45)	Cl(3)-B(14)	0.975(52)
Cl(3)-B(15)	0.756(47)	Cl(3)-B(16)	1.443(52)
Cl(3)-B(16a)	1.617(47)	Cl(5)-B(5)	1.133(26)
Cl(5)-B(4)	0.730(24)	Cl(5)-Cl(2a)	1.069(24)
Cl(6)-B(11)	0.825(27)	Cl(6)-B(12)	1.363(26)
Cl(6)-Cl(7)	0.576(29)	Cl(7)-B(5)	1.531(35)
Cl(7)-B(11)	1.250(30)	Cl(7)-B(12)	1.099(38)
Cl(4)-B(6)	1.896(30)	Cl(4)-B(1)	0.566(26)
Cl(4)-B(2)	0.931(28)	Cl(4)-B(13)	1.818(29)

Table 20. Bond angles for the 1,2,4 TMB-thiourea adduct structure.

Bond angles (°)

B(6)-B(5)-Cl(1)	154.0(23)	B(4)-B(5)-Cl(1)	86.0(22)
B(12)-B(5)-Cl(1)	97.9(29)	B(13)-B(5)-Cl(1)	154.0(25)
B(6)-B(5)-Cl(5)	151.3(12)	B(4)-B(5)-Cl(5)	31.4(12)
B(12)-B(5)-Cl(5)	151.1(30)	B(13)-B(5)-Cl(5)	151.1(17)
Cl(1)-B(5)-Cl(5)	54.6(25)	B(6)-B(5)-Cl(7)	102.1(14)
B(4)-B(5)-Cl(7)	137.7(14)	B(12)-B(5)-Cl(7)	45.8(17)
B(13)-B(5)-Cl(7)	101.8(16)	Cl(1)-B(5)-Cl(7)	52.2(25)
Cl(5)-B(5)-Cl(7)	106.6(22)	B(5)-B(6)-Cl(3)	128.4(19)
B(1)-B(6)-Cl(3)	111.4(18)	B(12)-B(6)-Cl(3)	83.8(21)
B(13)-B(6)-Cl(3)	55.0(44)	B(14)-B(6)-Cl(3)	31.8(18)
B(5)-B(6)-Cl(4)	110.8(9)	B(1)-B(6)-Cl(4)	9.2(9)
B(12)-B(6)-Cl(4)	153.5(21)	B(13)-B(6)-Cl(4)	70.8(45)
B(14)-B(6)-Cl(4)	88.9(14)	Cl(3)-B(6)-Cl(4)	120.6(22)
B(6)-B(1)-Cl(4)	147.5(35)	B(2)-B(1)-Cl(4)	27.5(35)
B(13)-B(1)-Cl(4)	157.5(47)	B(14)-B(1)-Cl(4)	156.6(39)
B(1)-B(2)-Cl(2)	168.5(12)	B(3)-B(2)-Cl(2)	71.4(12)
B(1)-B(2)-Cl(4)	16.3(21)	B(3)-B(2)-Cl(4)	136.3(20)
Cl(2)-B(2)-Cl(4)	152.2(28)	B(2)-B(3)-Cl(2)	65.0(10)
B(4)-B(3)-Cl(2)	174.8(9)	Cl(2)-B(3)-B(3a)	52.5(23)
Cl(2)-B(3)-Cl(2a)	148.1(14)	B(5)-B(4)-Cl(1)	47.6(19)
B(3)-B(4)-Cl(1)	167.5(20)	B(5)-B(4)-Cl(5)	54.1(21)
B(3)-B(4)-Cl(5)	173.4(23)	Cl(1)-B(4)-Cl(5)	6.6(24)
Cl(1)-B(4)-Cl(2a)	104.5(35)	Cl(5)-B(4)-Cl(2a)	97.9(37)
B(12)-B(11)-Cl(3)	73.6(13)	B(16)-B(11)-Cl(3)	46.4(13)
B(12)-B(11)-Cl(6)	70.5(17)	B(16)-B(11)-Cl(6)	169.2(16)
Cl(3)-B(11)-Cl(6)	144.1(23)	B(12)-B(11)-Cl(7)	48.7(17)
B(16)-B(11)-Cl(7)	167.6(19)	Cl(3)-B(11)-Cl(7)	122.2(22)
Cl(6)-B(11)-Cl(7)	22.0(20)	Cl(3)-B(11)-B(15a)	92.6(18)
Cl(6)-B(11)-B(15a)	123.2(27)	Cl(7)-B(11)-B(15a)	145.2(26)
Cl(3)-B(11)-B(16a)	48.7(15)	Cl(6)-B(11)-B(16a)	167.1(27)
Cl(7)-B(11)-B(16a)	170.8(25)	B(5)-B(12)-Cl(1)	49.6(25)
B(6)-B(12)-Cl(1)	127.3(25)	B(11)-B(12)-Cl(1)	102.4(19)
B(13)-B(12)-Cl(1)	136.5(20)	B(5)-B(12)-Cl(6)	117.3(22)
B(6)-B(12)-Cl(6)	160.2(21)	B(11)-B(12)-Cl(6)	34.8(10)
B(13)-B(12)-Cl(6)	154.7(11)	Cl(1)-B(12)-Cl(6)	67.9(22)
B(5)-B(12)-Cl(7)	93.2(24)	B(6)-B(12)-Cl(7)	165.7(26)
B(11)-B(12)-Cl(7)	58.8(15)	B(13)-B(12)-Cl(7)	174.3(20)
Cl(1)-B(12)-Cl(7)	43.8(24)	Cl(6)-B(12)-Cl(7)	24.1(15)
B(5)-B(13)-Cl(3)	120.8(22)	B(6)-B(13)-Cl(3)	116.3(48)
B(1)-B(13)-Cl(3)	129.2(27)	B(12)-B(13)-Cl(3)	84.7(20)
B(14)-B(13)-Cl(3)	35.3(20)	B(5)-B(13)-Cl(4)	102.4(12)
B(6)-B(13)-Cl(4)	100.0(45)	B(1)-B(13)-Cl(4)	6.8(14)
B(12)-B(13)-Cl(4)	139.1(9)	B(14)-B(13)-Cl(4)	100.7(9)
Cl(3)-B(13)-Cl(4)	136.0(24)	B(6)-B(14)-Cl(3)	85.1(32)
B(1)-B(14)-Cl(3)	129.5(34)	B(13)-B(14)-Cl(3)	88.8(32)
B(15)-B(14)-Cl(3)	31.3(32)	B(14)-B(15)-Cl(3)	42.0(44)
B(16)-B(15)-Cl(3)	78.1(44)	Cl(3)-B(15)-B(11a)	150.7(53)
Cl(3)-B(15)-B(16a)	100.0(50)	B(11)-B(16)-Cl(3)	89.2(21)
B(15)-B(16)-Cl(3)	30.8(21)	Cl(3)-B(16)-B(11a)	92.9(24)
Cl(3)-B(16)-B(15a)	168.4(34)	Cl(3)-B(16)-B(16a)	98.3(46)
Cl(3)-B(16)-Cl(3a)	160.3(14)	C(2)-S(2)-H(2)	103.7(43)
S(1)-C(1)-N(11)	119.9(7)	S(1)-C(1)-N(12)	120.8(6)
N(11)-C(1)-N(12)	119.2(9)	S(2)-C(2)-N(21)	121.8(7)
S(2)-C(2)-N(22)	119.5(7)	N(21)-C(2)-N(22)	118.7(9)
S(3)-C(3)-N(31)	121.6(5)	S(3)-C(3)-N(32)	120.1(6)
N(31)-C(3)-N(32)	118.2(7)	C(1)-N(11)-H(1)	117.3(26)
C(2)-N(21)-H(21)	131.0(54)	C(2)-N(21)-H(22)	131.7(65)
H(21)-N(21)-H(22)	97.3(83)	C(2)-N(22)-H(23)	117.4(62)
C(2)-N(22)-H(24)	139.3(51)	H(23)-N(22)-H(24)	85.8(86)
C(3)-N(31)-H(33)	131.6(48)	C(3)-N(31)-H(34)	114.4(39)
H(33)-N(31)-H(34)	110.9(71)	C(3)-N(32)-H(31)	111.0(49)
C(3)-N(32)-H(32)	114.4(45)	H(31)-N(32)-H(32)	130.9(57)
B(5)-Cl(1)-Cl(5)	50.3(28)	B(4)-Cl(1)-Cl(5)	4.0(15)
B(12)-Cl(1)-Cl(5)	82.5(37)	B(5)-Cl(1)-Cl(6)	75.8(27)
B(4)-Cl(1)-Cl(6)	121.9(36)	B(12)-Cl(1)-Cl(6)	43.3(15)
Cl(5)-Cl(1)-Cl(6)	125.9(46)	B(5)-Cl(1)-Cl(7)	68.2(34)
B(4)-Cl(1)-Cl(7)	114.3(45)	B(12)-Cl(1)-Cl(7)	35.7(23)
Cl(5)-Cl(1)-Cl(7)	118.3(55)	Cl(6)-Cl(1)-Cl(7)	7.6(18)
B(5)-Cl(5)-Cl(1)	75.1(31)	B(4)-Cl(5)-Cl(1)	169.4(38)
Cl(1)-Cl(5)-Cl(2a)	151.0(34)	B(11)-Cl(6)-Cl(1)	142.7(32)
B(12)-Cl(6)-Cl(1)	68.7(24)	B(11)-Cl(6)-Cl(7)	125.4(47)
B(12)-Cl(6)-Cl(7)	51.3(37)	Cl(1)-Cl(6)-Cl(7)	17.4(43)
B(5)-Cl(7)-Cl(1)	59.6(34)	B(11)-Cl(7)-Cl(1)	171.7(48)
B(12)-Cl(7)-Cl(1)	100.5(38)	B(5)-Cl(7)-Cl(6)	145.4(47)
B(11)-Cl(7)-Cl(6)	32.5(30)	B(12)-Cl(7)-Cl(6)	104.6(43)
Cl(1)-Cl(7)-Cl(6)	154.9(61)		

Table 21. F(obs) and sigma (F) for the 1,2,4 TCB-thiourea adduct structure.

F(obs) and sigma(F) (-sigma = unobserved): Trichlorobenzene Thiourea Adduct

h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s
2	0	0	88	1	5	3	0	18	1	1	6	0	28	1	10	8	0	8	2	0	12	0	42	1
4	0	0	41	1	6	3	0	6	2	2	6	0	46	1	11	8	0	3	-6	1	12	0	25	1
6	0	0	35	1	7	3	0	38	1	3	6	0	13	1	1	9	0	18	1	2	12	0	6	2
8	0	0	14	1	8	3	0	4	-3	4	6	0	44	1	2	9	0	86	1	3	12	0	9	1
10	0	0	24	1	9	3	0	9	2	5	6	0	45	1	3	9	0	7	1	4	12	0	4	-3
12	0	0	3	-6	10	3	0	3	-4	6	6	0	3	-4	4	9	0	3	-4	5	12	0	6	2
1	1	0	16	1	11	3	0	7	3	7	6	0	9	1	5	9	0	17	1	6	12	0	16	1
2	1	0	64	1	12	3	0	10	2	8	6	0	9	1	6	9	0	7	2	7	12	0	10	2
3	1	0	115	1	0	4	0	59	1	9	6	0	17	1	7	9	0	3	-4	8	12	0	3	-4
4	1	0	38	1	1	4	0	164	1	10	6	0	15	1	8	9	0	3	-4	10	12	0	8	2
5	1	0	36	1	2	4	0	102	1	11	6	0	6	-3	9	9	0	7	2	1	13	0	3	-4
6	1	0	25	1	3	4	0	28	1	12	6	0	3	-6	10	9	0	3	-6	2	13	0	6	2
7	1	0	30	1	4	4	0	6	1	1	7	0	8	1	11	9	0	3	-6	3	13	0	11	2
8	1	0	12	1	5	4	0	5	2	2	7	0	19	1	0	10	0	33	1	4	13	0	7	2
9	1	0	3	-4	6	4	0	3	-3	3	7	0	20	1	1	10	0	21	1	5	13	0	23	1
10	1	0	10	1	7	4	0	39	1	4	7	0	15	1	2	10	0	69	1	6	13	0	4	-3
11	1	0	6	-3	8	4	0	32	1	5	7	0	100	1	3	10	0	5	-2	7	13	0	6	-3
0	2	0	30	1	9	4	0	4	-3	6	7	0	11	2	4	10	0	3	-4	10	13	0	3	-7
1	2	0	4	1	10	4	0	16	1	7	7	0	18	2	5	10	0	12	1	0	14	0	31	1
2	2	0	13	1	11	4	0	3	-6	8	7	0	16	2	6	10	0	3	-4	1	14	0	19	1
3	2	0	92	1	12	4	0	3	-6	9	7	0	3	-4	7	10	0	7	2	2	14	0	13	1
4	2	0	10	1	1	5	0	37	1	10	7	0	5	-3	8	10	0	15	1	3	14	0	4	-3
5	2	0	6	1	2	5	0	92	1	11	7	0	6	-3	9	10	0	3	-4	4	14	0	3	-4
6	2	0	3	-3	3	5	0	25	1	12	7	0	3	-6	10	10	0	3	-6	5	14	0	10	2
7	2	0	62	1	4	5	0	69	1	0	8	0	103	1	11	10	0	3	-6	6	14	0	4	-3
8	2	0	3	-4	5	5	0	69	1	1	8	0	4	-2	1	11	0	25	1	1	15	0	9	2
9	2	0	8	1	6	5	0	7	1	2	8	0	110	1	2	11	0	32	1	2	15	0	12	2
10	2	0	7	2	7	5	0	6	2	3	8	0	16	1	3	11	0	17	1	3	15	0	24	1
11	2	0	3	-6	8	5	0	15	1	4	8	0	34	1	4	11	0	13	1	4	15	0	7	2
12	2	0	3	-6	9	5	0	9	1	5	8	0	7	2	5	11	0	45	1	5	15	0	6	2
1	3	0	12	1	10	5	0	11	1	6	8	0	6	2	6	11	0	4	-3	6	15	0	9	2
2	3	0	68	1	11	5	0	7	3	7	8	0	16	1	7	11	0	3	-4	0	16	0	7	2
3	3	0	150	1	12	5	0	3	-6	8	8	0	24	1	8	11	0	3	-4	1	16	0	7	2
4	3	0	8	1	0	6	0	45	1	9	8	0	9	2	10	11	0	3	-6	2	16	0	6	2

Table 21. (Continued)

F(obs) and sigma(F) (-sigma = unobserved): Trichlorobenzene Thiourea Adduct

h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s
3	16	0	10	1	3	1	1	8	1	-10	3	1	10	2	1	4	1	23	1	12	5	1	10	2
4	16	0	5	-3	4	1	1	32	1	-9	3	1	17	1	2	4	1	54	1	-10	6	1	8	2
5	16	0	4	-3	5	1	1	39	1	-8	3	1	3	-5	3	4	1	29	1	-9	6	1	12	1
1	17	0	5	-3	6	1	1	17	1	-7	3	1	20	1	4	4	1	58	1	-8	6	1	9	2
2	17	0	3	-4	7	1	1	7	2	-6	3	1	75	1	5	4	1	60	1	-7	6	1	3	-5
3	17	0	10	1	8	1	1	9	2	-5	3	1	17	1	6	4	1	47	1	-6	6	1	31	1
0	18	0	20	1	9	1	1	21	1	-4	3	1	27	1	7	4	1	10	1	-5	6	1	35	1
1	18	0	3	-6	10	1	1	7	2	-3	3	1	69	1	8	4	1	3	-5	-4	6	1	24	1
-10	0	1	3	-6	11	1	1	9	2	-2	3	1	137	1	9	4	1	10	2	-3	6	1	157	1
-8	0	1	10	2	12	1	1	3	-6	-1	3	1	333	1	10	4	1	3	-6	-2	6	1	21	1
-6	0	1	18	1	-11	2	1	14	1	0	3	1	29	1	11	4	1	3	-6	-1	6	1	29	1
-4	0	1	160	1	-10	2	1	3	-6	1	3	1	32	1	12	4	1	7	-3	0	6	1	72	1
-2	0	1	27	1	-9	2	1	3	-5	2	3	1	26	1	-10	5	1	15	1	1	6	1	16	1
0	0	1	2	-1	-8	2	1	10	2	3	3	1	41	1	-9	5	1	6	-3	2	6	1	29	1
2	0	1	134	1	-7	2	1	6	2	4	3	1	26	1	-8	5	1	33	1	3	6	1	66	1
4	0	1	84	1	-6	2	1	2	-5	5	3	1	11	1	-7	5	1	10	1	4	6	1	11	1
6	0	1	60	1	-5	2	1	73	1	6	3	1	5	-2	-6	5	1	60	1	5	6	1	2	-5
8	0	1	3	-5	-4	2	1	74	1	7	3	1	3	-5	-5	5	1	11	1	6	6	1	28	1
10	0	1	3	-6	-3	2	1	72	1	8	3	1	6	2	-4	5	1	20	1	7	6	1	35	1
12	0	1	10	2	-2	2	1	72	1	9	3	1	35	1	-3	5	1	2	-4	8	6	1	3	-6
-11	1	1	3	-6	-1	2	1	79	1	10	3	1	6	-3	-2	5	1	19	1	9	6	1	9	2
-10	1	1	8	2	0	2	1	3	1	11	3	1	10	2	-1	5	1	48	1	10	6	1	9	2
-9	1	1	10	1	1	2	1	20	1	12	3	1	3	-6	0	5	1	147	1	11	6	1	6	-4
-8	1	1	72	1	2	2	1	73	1	-10	4	1	14	1	1	5	1	112	1	-10	7	1	3	-6
-7	1	1	2	-5	3	2	1	96	1	-9	4	1	8	2	2	5	1	102	1	-9	7	1	11	2
-6	1	1	49	1	4	2	1	25	1	-8	4	1	9	2	3	5	1	14	1	-8	7	1	17	1
-5	1	1	46	1	5	2	1	82	1	-7	4	1	3	-5	4	5	1	2	-4	-7	7	1	5	-3
-4	1	1	27	1	6	2	1	13	1	-6	4	1	39	1	5	5	1	12	1	-6	7	1	34	1
-3	1	1	57	1	7	2	1	30	1	-5	4	1	23	1	6	5	1	3	-5	-5	7	1	4	-3
-2	1	1	13	1	8	2	1	3	-5	-4	4	1	45	1	7	5	1	36	1	-4	7	1	7	2
-1	1	1	22	1	9	2	1	3	-6	-3	4	1	49	1	8	5	1	7	2	-3	7	1	58	1
0	1	1	3	1	10	2	1	3	-6	-2	4	1	63	1	9	5	1	6	-3	-2	7	1	39	1
1	1	1	21	1	11	2	1	7	-3	-1	4	1	341	1	10	5	1	8	2	-1	7	1	33	1
2	1	1	229	1	12	2	1	9	2	0	4	1	78	1	11	5	1	3	-6	0	7	1	58	1

Table 21. (Continued)

F(obs) and sigma(F) (-sigma = unobserved): Trichlorobenzene Thiourea Adduct

h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s
1	7	1	109	1	-7	9	1	3	-5	6	10	1	3	-5	3	12	1	5	-3	6	14	1	7	3
2	7	1	12	1	-6	9	1	49	1	7	10	1	3	-6	4	12	1	3	-6	-6	15	1	10	2
3	7	1	8	1	-5	9	1	28	1	8	10	1	3	-6	5	12	1	10	2	-5	15	1	11	2
4	7	1	5	-3	-4	9	1	4	-3	10	10	1	3	-6	6	12	1	7	2	-4	15	1	9	2
5	7	1	12	1	-3	9	1	3	-5	11	10	1	3	-6	7	12	1	12	2	-3	15	1	3	-6
6	7	1	27	1	-2	9	1	17	1	-8	11	1	3	-6	10	12	1	3	-6	-2	15	1	10	2
7	7	1	32	1	-1	9	1	16	1	-7	11	1	3	-6	-7	13	1	11	2	-1	15	1	22	1
8	7	1	5	-3	0	9	1	91	1	-6	11	1	17	1	-6	13	1	3	-6	0	15	1	14	1
9	7	1	15	1	1	9	1	6	2	-5	11	1	3	-5	-5	13	1	3	-6	1	15	1	4	-4
10	7	1	8	2	2	9	1	12	1	-4	11	1	19	1	-4	13	1	12	1	2	15	1	14	1
11	7	1	7	-3	3	9	1	22	1	-3	11	1	3	-5	-3	13	1	3	-6	3	15	1	10	2
-9	8	1	3	-6	4	9	1	45	1	-2	11	1	15	1	-2	13	1	15	1	4	15	1	3	-6
-8	8	1	14	1	5	9	1	12	1	-1	11	1	31	1	-1	13	1	3	-5	5	15	1	8	2
-7	8	1	5	-3	6	9	1	7	2	0	11	1	17	1	0	13	1	8	2	-5	16	1	9	2
-6	8	1	28	1	7	9	1	6	-3	1	11	1	45	1	1	13	1	35	1	-4	16	1	3	-6
-5	8	1	9	2	8	9	1	6	-3	2	11	1	12	1	2	13	1	27	1	-3	16	1	3	-6
-4	8	1	2	-5	9	9	1	8	2	3	11	1	3	-6	3	13	1	6	-3	-2	16	1	3	-6
-3	8	1	89	1	10	9	1	9	2	4	11	1	14	1	4	13	1	17	1	-1	16	1	17	1
-2	8	1	54	1	11	9	1	10	2	5	11	1	3	-5	5	13	1	15	1	0	16	1	4	-4
-1	8	1	7	1	-9	10	1	3	-6	6	11	1	8	2	6	13	1	10	2	1	16	1	3	-6
0	8	1	38	1	-8	10	1	3	-6	7	11	1	16	1	7	13	1	14	1	2	16	1	13	1
1	8	1	36	1	-7	10	1	9	2	8	11	1	11	2	-7	14	1	9	2	3	16	1	3	-6
2	8	1	7	1	-6	10	1	37	1	10	11	1	5	-4	-6	14	1	7	3	4	16	1	3	-6
3	8	1	26	1	-5	10	1	3	-5	-8	12	1	8	2	-5	14	1	9	2	-4	17	1	11	2
4	8	1	76	1	-4	10	1	4	-4	-7	12	1	3	-6	-4	14	1	12	1	-3	17	1	8	2
5	8	1	13	1	-3	10	1	25	1	-6	12	1	3	-6	-3	14	1	17	1	-2	17	1	8	2
6	8	1	6	2	-2	10	1	11	1	-5	12	1	10	1	-2	14	1	3	-6	-1	17	1	13	2
7	8	1	35	1	-1	10	1	32	1	-4	12	1	10	2	-1	14	1	24	1	0	17	1	6	-3
8	8	1	4	-4	0	10	1	4	-3	-3	12	1	54	1	0	14	1	3	-5	1	17	1	3	-6
9	8	1	3	-6	1	10	1	20	1	-2	12	1	8	2	1	14	1	10	2	2	17	1	9	2
10	8	1	3	-6	2	10	1	3	-5	-1	12	1	8	2	2	14	1	10	2	3	17	1	5	-4
11	8	1	8	3	3	10	1	25	1	0	12	1	11	1	3	14	1	3	-6	-1	18	1	3	-6
-9	9	1	3	-6	4	10	1	69	1	1	12	1	4	-4	4	14	1	16	1	0	18	1	6	-3
-8	9	1	6	-3	5	10	1	10	2	2	12	1	6	2	5	14	1	7	3	1	18	1	8	2

Table 21. (Continued)

F(obs) and sigma(F) (-sigma = unobserved): Trichlorobenzene Thiourea Adduct

h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s
-10	0	2	3	-5	11	1	2	9	2	-3	3	2	115	1	9	4	2	5	-3	2	6	2	8	1
-8	0	2	14	1	12	1	2	5	-4	-2	3	2	341	1	11	4	2	9	2	3	6	2	38	1
-6	0	2	73	1	-11	2	2	3	-6	-1	3	2	4	2	-10	5	2	6	-3	4	6	2	32	1
-4	0	2	6	1	-10	2	2	6	-3	0	3	2	46	1	-9	5	2	19	1	5	6	2	34	1
-2	0	2	235	1	-9	2	2	37	1	1	3	2	45	1	-8	5	2	3	-5	6	6	2	14	1
0	0	2	19	1	-8	2	2	17	1	2	3	2	78	1	-7	5	2	28	1	7	6	2	6	-3
2	0	2	30	1	-7	2	2	22	1	3	3	2	27	1	-6	5	2	28	1	8	6	2	16	1
4	0	2	94	1	-6	2	2	41	1	4	3	2	24	1	-5	5	2	5	-2	9	6	2	15	1
6	0	2	16	1	-5	2	2	33	1	5	3	2	31	1	-4	5	2	118	1	10	6	2	3	-6
8	0	2	44	1	-4	2	2	66	1	6	3	2	43	1	-3	5	2	49	1	11	6	2	3	-6
10	0	2	7	2	-3	2	2	79	1	7	3	2	13	1	-2	5	2	36	1	-10	7	2	11	2
12	0	2	3	-6	-2	2	2	114	1	8	3	2	5	-3	-1	5	2	121	1	-9	7	2	3	-6
-11	1	2	7	2	-1	2	2	38	1	9	3	2	7	3	0	5	2	14	1	-8	7	2	3	-5
-10	1	2	3	-6	0	2	2	93	1	11	3	2	7	-3	1	5	2	32	1	-7	7	2	3	-5
-9	1	2	18	1	1	2	2	270	1	-11	4	2	8	2	2	5	2	2	-4	-6	7	2	7	2
-8	1	2	7	2	2	2	2	151	1	-10	4	2	3	-6	3	5	2	18	1	-5	7	2	8	2
-7	1	2	11	1	3	2	2	89	1	-9	4	2	13	1	4	5	2	38	1	-4	7	2	8	1
-6	1	2	39	1	4	2	2	62	1	-8	4	2	13	1	5	5	2	6	2	-3	7	2	9	1
-5	1	2	30	1	5	2	2	2	-5	-7	4	2	13	1	6	5	2	51	1	-2	7	2	90	1
-4	1	2	24	1	6	2	2	2	-5	-6	4	2	49	1	7	5	2	4	-3	-1	7	2	150	1
-3	1	2	112	1	7	2	2	3	-5	-5	4	2	42	1	8	5	2	18	1	0	7	2	56	1
-2	1	2	241	1	8	2	2	25	1	-4	4	2	51	1	9	5	2	3	-6	1	7	2	7	1
-1	1	2	8	1	9	2	2	15	1	-3	4	2	82	1	-10	6	2	3	-6	2	7	2	14	1
0	1	2	30	1	10	2	2	6	-3	-2	4	2	83	1	-9	6	2	9	2	3	7	2	55	1
1	1	2	25	1	11	2	2	13	2	-1	4	2	5	2	-8	6	2	5	-3	4	7	2	17	1
2	1	2	20	1	12	2	2	10	2	0	4	2	9	1	-7	6	2	59	1	5	7	2	14	1
3	1	2	17	1	-11	3	2	10	2	1	4	2	154	1	-6	6	2	53	1	6	7	2	22	1
4	1	2	143	1	-10	3	2	5	-3	2	4	2	74	1	-5	6	2	5	-2	7	7	2	3	-6
5	1	2	30	1	-9	3	2	32	1	3	4	2	10	1	-4	6	2	2	-5	8	7	2	6	-3
6	1	2	2	-5	-8	3	2	3	-5	4	4	2	40	1	-3	6	2	11	1	9	7	2	12	2
7	1	2	12	1	-7	3	2	24	1	5	4	2	2	-5	-2	6	2	3	-3	10	7	2	3	-6
8	1	2	26	1	-6	3	2	42	1	6	4	2	9	2	-1	6	2	147	1	11	7	2	3	-6
9	1	2	6	2	-5	3	2	24	1	7	4	2	3	-5	0	6	2	28	1	-10	8	2	3	-6
10	1	2	3	-6	-4	3	2	68	1	8	4	2	10	2	1	6	2	28	1	-9	8	2	9	2

Table 21. (Continued)

F(obs) and sigma(F) (-sigma = unobserved): Trichlorobenzene Thiourea Adduct

h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s
-8	8	2	21	1	6	9	2	60	1	2	11	2	6	2	3	13	2	20	1	-1	16	2	8	2
-7	8	2	31	1	7	9	2	3	-6	3	11	2	26	1	4	13	2	18	1	0	16	2	3	-6
-6	8	2	3	-5	8	9	2	16	1	4	11	2	12	1	5	13	2	8	2	1	16	2	27	1
-5	8	2	6	2	10	9	2	3	-6	5	11	2	3	-6	6	13	2	5	-4	2	16	2	3	-6
-4	8	2	37	1	-9	10	2	10	2	6	11	2	28	1	-7	14	2	5	-4	3	16	2	3	-6
-3	8	2	11	1	-8	10	2	11	2	7	11	2	3	-6	-6	14	2	15	1	4	16	2	4	-4
-2	8	2	24	1	-7	10	2	10	2	10	11	2	3	-6	-5	14	2	18	1	-4	17	2	3	-6
-1	8	2	54	1	-6	10	2	7	2	-8	12	2	3	-6	-4	14	2	5	-3	-3	17	2	7	-3
0	8	2	52	1	-5	10	2	11	1	-7	12	2	11	2	-3	14	2	14	1	-2	17	2	16	1
1	8	2	29	1	-4	10	2	40	1	-6	12	2	13	1	-2	14	2	3	-6	-1	17	2	3	-6
2	8	2	6	2	-3	10	2	7	2	-5	12	2	3	-5	-1	14	2	8	2	0	17	2	7	3
3	8	2	54	1	-2	10	2	46	1	-4	12	2	3	-6	0	14	2	3	-5	1	17	2	3	-6
4	8	2	7	2	-1	10	2	42	1	-3	12	2	7	2	1	14	2	23	1	2	17	2	3	-6
5	8	2	4	-3	0	10	2	40	1	-2	12	2	3	-5	2	14	2	12	1	3	17	2	3	-6
6	8	2	18	1	1	10	2	15	1	-1	12	2	37	1	3	14	2	8	2	-1	18	2	6	-3
7	8	2	7	2	2	10	2	56	1	0	12	2	14	1	4	14	2	18	1	0	18	2	3	-6
8	8	2	3	-6	3	10	2	36	1	1	12	2	7	2	5	14	2	3	-6	-10	0	3	30	1
10	8	2	3	-6	4	10	2	19	1	2	12	2	5	-3	6	14	2	3	-6	-8	0	3	7	2
11	8	2	3	-6	5	10	2	3	-5	3	12	2	45	1	-6	15	2	6	-3	-6	0	3	13	1
-9	9	2	4	-4	6	10	2	3	-6	4	12	2	6	-3	-5	15	2	3	-6	-4	0	3	170	1
-8	9	2	3	-6	7	10	2	5	-4	5	12	2	6	-3	-4	15	2	12	2	-2	0	3	151	1
-7	9	2	16	1	8	10	2	3	-6	6	12	2	6	-3	-3	15	2	12	1	0	0	3	211	4
-6	9	2	8	2	10	10	2	3	-6	7	12	2	10	2	-2	15	2	5	-3	2	0	3	17	1
-5	9	2	7	2	-9	11	2	8	2	-8	13	2	5	-4	-1	15	2	7	2	4	0	3	42	1
-4	9	2	80	1	-8	11	2	10	2	-7	13	2	3	-6	0	15	2	5	-3	6	0	3	37	1
-3	9	2	2	-5	-7	11	2	5	-3	-6	13	2	9	2	1	15	2	4	-4	8	0	3	22	1
-2	9	2	6	2	-6	11	2	3	-5	-5	13	2	3	-6	2	15	2	5	-3	-11	1	3	3	-6
-1	9	2	48	1	-5	11	2	4	-4	-4	13	2	18	1	3	15	2	10	2	-10	1	3	3	-6
0	9	2	46	1	-4	11	2	29	1	-3	13	2	11	1	4	15	2	8	2	-9	1	3	8	2
1	9	2	20	1	-3	11	2	6	2	-2	13	2	32	1	5	15	2	9	2	-8	1	3	13	1
2	9	2	7	2	-2	11	2	3	-5	-1	13	2	35	1	-5	16	2	8	2	-7	1	3	56	1
3	9	2	4	-4	-1	11	2	23	1	0	13	2	22	1	-4	16	2	7	2	-6	1	3	12	1
4	9	2	11	1	0	11	2	3	-5	1	13	2	3	-5	-3	16	2	5	-4	-5	1	3	69	1
5	9	2	3	-5	1	11	2	21	1	2	13	2	11	1	-2	16	2	8	2	-4	1	3	131	1

Table 21. (Continued)

F(obs) and sigma(F) (-sigma = unobserved): Trichlorobenzene Thiourea Adduct

h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s
-3	1	3	142	1	9	2	3	3	-6	-1	4	3	2	-4	-10	6	3	11	2	2	7	3	6	2
-2	1	3	28	1	11	2	3	9	2	0	4	3	95	1	-9	6	3	26	1	3	7	3	31	1
-1	1	3	63	1	-11	3	3	3	-6	1	4	3	17	1	-8	6	3	13	1	4	7	3	33	1
0	1	3	183	1	-10	3	3	7	2	2	4	3	13	1	-7	6	3	29	1	5	7	3	33	1
1	1	3	24	1	-9	3	3	13	1	3	4	3	2	-5	-6	6	3	17	1	6	7	3	3	-5
2	1	3	7	1	-8	3	3	11	1	4	4	3	15	1	-5	6	3	36	1	7	7	3	10	2
3	1	3	59	1	-7	3	3	85	1	5	4	3	20	1	-4	6	3	29	1	8	7	3	9	2
4	1	3	25	1	-6	3	3	9	1	6	4	3	25	1	-3	6	3	111	1	10	7	3	3	-6
5	1	3	21	1	-5	3	3	10	1	7	4	3	30	1	-2	6	3	67	1	-10	8	3	10	2
6	1	3	12	1	-4	3	3	82	1	8	4	3	22	1	-1	6	3	5	2	-9	8	3	11	2
7	1	3	5	-3	-3	3	3	29	1	9	4	3	4	-4	0	6	3	89	1	-8	8	3	19	1
8	1	3	9	2	-2	3	3	81	1	11	4	3	5	-4	1	6	3	33	1	-7	8	3	3	-5
9	1	3	5	-3	-1	3	3	2	-4	-11	5	3	9	2	2	6	3	11	1	-6	8	3	3	-5
11	1	3	3	-6	0	3	3	10	1	-10	5	3	3	-6	3	6	3	4	-3	-5	8	3	29	1
-11	2	3	10	2	1	3	3	18	1	-9	5	3	6	-3	4	6	3	9	1	-4	8	3	9	1
-10	2	3	14	1	2	3	3	89	1	-8	5	3	29	1	5	6	3	68	1	-3	8	3	8	1
-9	2	3	8	2	3	3	3	185	1	-7	5	3	20	1	6	6	3	19	1	-2	8	3	112	1
-8	2	3	6	2	4	3	3	21	1	-6	5	3	9	1	7	6	3	3	-6	-1	8	3	26	1
-7	2	3	22	1	5	3	3	12	1	-5	5	3	68	1	8	6	3	14	1	0	8	3	11	1
-6	2	3	2	-5	6	3	3	3	-5	-4	5	3	48	1	9	6	3	7	2	1	8	3	43	1
-5	2	3	25	1	7	3	3	17	1	-3	5	3	52	1	10	6	3	3	-6	2	8	3	10	1
-4	2	3	43	1	8	3	3	12	1	-2	5	3	54	1	11	6	3	3	-7	3	8	3	11	1
-3	2	3	15	1	9	3	3	6	-3	-1	5	3	24	1	-10	7	3	3	-6	4	8	3	18	1
-2	2	3	163	1	11	3	3	3	-6	0	5	3	122	1	-9	7	3	15	1	5	8	3	41	1
-1	2	3	7	1	-11	4	3	8	2	1	5	3	6	2	-8	7	3	7	2	6	8	3	3	-6
0	2	3	95	1	-10	4	3	12	1	2	5	3	24	1	-7	7	3	18	1	7	8	3	3	-6
1	2	3	4	2	-9	4	3	9	2	3	5	3	18	1	-6	7	3	3	-5	8	8	3	11	2
2	2	3	25	1	-8	4	3	13	1	4	5	3	4	-3	-5	7	3	61	1	10	8	3	3	-6
3	2	3	50	1	-7	4	3	23	1	5	5	3	14	1	-4	7	3	19	1	-10	9	3	7	3
4	2	3	22	1	-6	4	3	15	1	6	5	3	3	-5	-3	7	3	113	1	-9	9	3	3	-6
5	2	3	25	1	-5	4	3	59	1	7	5	3	22	1	-2	7	3	4	-3	-8	9	3	7	2
6	2	3	9	2	-4	4	3	39	1	8	5	3	3	-6	-1	7	3	28	1	-7	9	3	3	-5
7	2	3	47	1	-3	4	3	84	1	9	5	3	7	2	0	7	3	30	1	-6	9	3	18	1
8	2	3	5	-3	-2	4	3	234	1	11	5	3	5	-4	1	7	3	93	1	-5	9	3	10	1

Table 21. (Continued)

F(obs) and sigma(F) (-sigma = unobserved): Trichlorobenzene Thiourea Adduct

h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s
-4	9	3	12	1	-7	11	3	13	1	-4	13	3	6	-3	-5	16	3	3	-6	-3	1	4	42	1
-3	9	3	35	1	-6	11	3	16	1	-3	13	3	24	1	-4	16	3	3	-6	-2	1	4	109	1
-2	9	3	2	-5	-5	11	3	39	1	-2	13	3	6	2	-3	16	3	11	2	-1	1	4	137	1
-1	9	3	26	1	-4	11	3	3	-5	-1	13	3	6	2	-2	16	3	3	-6	0	1	4	81	1
0	9	3	4	-3	-3	11	3	3	-5	0	13	3	16	1	-1	16	3	6	-3	1	1	4	16	1
1	9	3	7	2	-2	11	3	17	1	1	13	3	11	1	0	16	3	7	3	2	1	4	33	1
2	9	3	80	1	-1	11	3	3	-5	2	13	3	19	1	1	16	3	9	2	3	1	4	6	2
3	9	3	11	1	0	11	3	15	1	3	13	3	4	-4	2	16	3	3	-6	4	1	4	3	-3
4	9	3	3	-5	1	11	3	46	1	4	13	3	3	-6	3	16	3	9	2	5	1	4	32	1
5	9	3	8	2	2	11	3	37	1	5	13	3	10	2	-4	17	3	10	2	6	1	4	39	1
6	9	3	5	-3	3	11	3	8	2	-7	14	3	8	2	-3	17	3	3	-6	7	1	4	21	1
7	9	3	5	-3	4	11	3	15	1	-6	14	3	3	-6	-2	17	3	3	-6	8	1	4	11	2
8	9	3	16	1	5	11	3	28	1	-5	14	3	3	-6	-1	17	3	3	-6	9	1	4	10	2
10	9	3	3	-7	6	11	3	7	3	-4	14	3	13	1	0	17	3	5	-4	11	1	4	3	-6
-9	10	3	3	-6	7	11	3	3	-6	-3	14	3	11	1	1	17	3	3	-6	-11	2	4	3	-6
-8	10	3	8	2	-8	12	3	3	-6	-2	14	3	24	1	2	17	3	8	2	-10	2	4	15	1
-7	10	3	3	-5	-7	12	3	3	-6	-1	14	3	3	-6	-10	0	4	16	1	-9	2	4	3	-5
-6	10	3	9	2	-6	12	3	11	1	0	14	3	17	1	-8	0	4	51	1	-8	2	4	10	2
-5	10	3	13	1	-5	12	3	13	1	1	14	3	15	1	-6	0	4	49	1	-7	2	4	25	1
-4	10	3	9	2	-4	12	3	23	1	2	14	3	10	2	-4	0	4	67	1	-6	2	4	29	1
-3	10	3	5	-3	-3	12	3	3	-5	3	14	3	9	2	-2	0	4	54	1	-5	2	4	101	1
-2	10	3	86	1	-2	12	3	14	1	4	14	3	3	-6	0	0	4	124	2	-4	2	4	44	1
-1	10	3	14	1	-1	12	3	16	1	5	14	3	10	2	2	0	4	96	1	-3	2	4	5	1
0	10	3	17	1	0	12	3	31	1	-6	15	3	6	-3	4	0	4	24	1	-2	2	4	57	1
1	10	3	9	2	1	12	3	17	1	-5	15	3	5	-3	6	0	4	16	1	-1	2	4	24	1
2	10	3	12	1	2	12	3	26	1	-4	15	3	9	2	8	0	4	3	-6	0	2	4	42	1
3	10	3	3	-5	3	12	3	3	-6	-3	15	3	11	2	-11	1	4	8	2	1	2	4	4	-2
4	10	3	3	-5	4	12	3	5	-3	-2	15	3	6	-3	-10	1	4	3	-6	2	2	4	42	1
5	10	3	15	1	5	12	3	30	1	-1	15	3	5	-4	-9	1	4	9	2	3	2	4	2	-5
6	10	3	3	-6	6	12	3	9	2	0	15	3	11	2	-8	1	4	70	1	4	2	4	15	1
7	10	3	8	2	-8	13	3	3	-6	1	15	3	3	-6	-7	1	4	10	1	5	2	4	50	1
10	10	3	3	-7	-7	13	3	3	-6	2	15	3	3	-6	-6	1	4	13	1	6	2	4	3	-5
-9	11	3	7	-3	-6	13	3	6	-3	3	15	3	23	1	-5	1	4	51	1	7	2	4	7	2
-8	11	3	3	-6	-5	13	3	20	1	4	15	3	8	2	-4	1	4	23	1	8	2	4	10	2

Table 21. (Continued)

F(obs) and sigma(F) (-sigma = unobserved): Trichlorobenzene Thiourea Adduct

h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s
9	2	4	8	2	-1	4	4	27	1	-7	6	4	16	1	7	7	4	35	1	1	9	4	3	-5
11	2	4	3	-6	0	4	4	35	1	-6	6	4	3	-5	8	7	4	5	-3	2	9	4	3	-5
-11	3	4	9	2	1	4	4	72	1	-5	6	4	12	1	10	7	4	3	-6	3	9	4	26	1
-10	3	4	20	1	2	4	4	129	1	-4	6	4	21	1	-10	8	4	4	-4	4	9	4	16	1
-9	3	4	10	1	3	4	4	37	1	-3	6	4	88	1	-9	8	4	3	-6	5	9	4	5	-3
-8	3	4	27	1	4	4	4	47	1	-2	6	4	12	1	-8	8	4	14	1	6	9	4	5	-3
-7	3	4	3	-5	5	4	4	23	1	-1	6	4	8	1	-7	8	4	19	1	7	9	4	5	-4
-6	3	4	20	1	6	4	4	14	1	0	6	4	5	2	-6	8	4	33	1	10	9	4	7	-3
-5	3	4	2	-5	7	4	4	18	1	1	6	4	34	1	-5	8	4	6	2	-9	10	4	7	2
-4	3	4	42	1	8	4	4	7	2	2	6	4	102	1	-4	8	4	29	1	-8	10	4	12	1
-3	3	4	63	1	11	4	4	9	2	3	6	4	33	1	-3	8	4	44	1	-7	10	4	3	-5
-2	3	4	5	1	-11	5	4	5	-4	4	6	4	18	1	-2	8	4	5	-3	-6	10	4	39	1
-1	3	4	201	1	-10	5	4	24	1	5	6	4	3	-5	-1	8	4	18	1	-5	10	4	17	1
0	3	4	98	1	-9	5	4	7	2	6	6	4	7	2	0	8	4	5	-2	-4	10	4	7	2
1	3	4	42	1	-8	5	4	27	1	7	6	4	3	-6	1	8	4	69	1	-3	10	4	20	1
2	3	4	15	1	-7	5	4	7	2	8	6	4	3	-6	2	8	4	12	1	-2	10	4	10	1
3	3	4	7	1	-6	5	4	14	1	10	6	4	3	-6	3	8	4	49	1	-1	10	4	7	2
4	3	4	17	1	-5	5	4	44	1	-10	7	4	9	2	4	8	4	48	1	0	10	4	39	1
5	3	4	47	1	-4	5	4	10	1	-9	7	4	3	-6	5	8	4	3	-5	1	10	4	9	2
6	3	4	6	-2	-3	5	4	53	1	-8	7	4	9	2	6	8	4	3	-6	2	10	4	16	1
7	3	4	15	1	-2	5	4	30	1	-7	7	4	3	-5	7	8	4	7	-3	3	10	4	6	-3
8	3	4	3	-6	-1	5	4	45	1	-6	7	4	25	1	8	8	4	3	-6	4	10	4	43	1
9	3	4	13	2	0	5	4	20	1	-5	7	4	8	2	10	8	4	3	-7	5	10	4	7	2
11	3	4	3	-6	1	5	4	57	1	-4	7	4	63	1	-10	9	4	22	1	6	10	4	3	-6
-11	4	4	3	-6	2	5	4	50	1	-3	7	4	107	1	-9	9	4	10	2	7	10	4	3	-6
-10	4	4	3	-6	3	5	4	15	1	-2	7	4	10	1	-8	9	4	8	2	-9	11	4	7	3
-9	4	4	3	-5	4	5	4	28	1	-1	7	4	23	1	-7	9	4	3	-5	-8	11	4	10	2
-8	4	4	27	1	5	5	4	11	1	0	7	4	7	1	-6	9	4	18	1	-7	11	4	4	-4
-7	4	4	5	-2	6	5	4	9	2	1	7	4	39	1	-5	9	4	6	-2	-6	11	4	8	2
-6	4	4	53	1	7	5	4	23	1	2	7	4	6	2	-4	9	4	11	1	-5	11	4	14	1
-5	4	4	110	1	8	5	4	3	-6	3	7	4	3	-5	-3	9	4	23	1	-4	11	4	18	1
-4	4	4	53	1	-10	6	4	5	-4	4	7	4	7	2	-2	9	4	2	-5	-3	11	4	42	1
-3	4	4	84	1	-9	6	4	3	-6	5	7	4	12	1	-1	9	4	11	1	-2	11	4	5	-3
-2	4	4	40	1	-8	6	4	17	1	6	7	4	6	-3	0	9	4	67	1	-1	11	4	9	2

Table 21. (Continued)

F(obs) and sigma(F) (-sigma = unobserved): Trichlorobenzene Thiourea Adduct

h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s
0	11	4	54	1	4	13	4	3	-6	3	16	4	3	-6	7	1	5	12	1	1	3	5	126	1
1	11	4	31	1	5	13	4	9	2	-3	17	4	10	2	8	1	5	3	-6	2	3	5	43	1
2	11	4	5	-3	-7	14	4	5	-4	-2	17	4	7	-3	-11	2	5	21	1	3	3	5	15	1
3	11	4	11	2	-6	14	4	7	3	-1	17	4	10	2	-10	2	5	3	-6	4	3	5	11	1
4	11	4	17	1	-5	14	4	6	-3	0	17	4	3	-6	-9	2	5	38	1	5	3	5	3	-5
5	11	4	3	-6	-4	14	4	8	2	1	17	4	3	-6	-8	2	5	10	1	6	3	5	13	1
6	11	4	6	-3	-3	14	4	13	1	-10	0	5	5	-3	-7	2	5	12	1	7	3	5	4	-4
-8	12	4	3	-6	-2	14	4	7	2	-8	0	5	26	1	-6	2	5	45	1	8	3	5	10	2
-7	12	4	7	2	-1	14	4	12	1	-6	0	5	35	1	-5	2	5	38	1	-11	4	5	7	2
-6	12	4	3	-6	0	14	4	21	1	-4	0	5	2	-4	-4	2	5	24	1	-10	4	5	6	-3
-5	12	4	10	2	1	14	4	5	-3	-2	0	5	94	1	-3	2	5	96	1	-9	4	5	25	1
-4	12	4	21	1	2	14	4	17	1	0	0	5	88	1	-2	2	5	48	1	-8	4	5	26	1
-3	12	4	44	1	3	14	4	8	2	2	0	5	10	1	-1	2	5	41	1	-7	4	5	33	1
-2	12	4	12	1	4	14	4	14	1	4	0	5	16	1	0	2	5	107	1	-6	4	5	6	2
-1	12	4	12	1	5	14	4	6	-3	6	0	5	4	-4	1	2	5	118	1	-5	4	5	48	1
0	12	4	23	1	-6	15	4	3	-6	8	0	5	28	1	2	2	5	21	1	-4	4	5	47	1
1	12	4	19	1	-5	15	4	3	-6	-11	1	5	7	2	3	2	5	5	-2	-3	4	5	25	1
2	12	4	19	1	-4	15	4	6	-3	-10	1	5	9	2	4	2	5	11	1	-2	4	5	54	1
3	12	4	21	1	-3	15	4	9	2	-9	1	5	3	-5	5	2	5	7	2	-1	4	5	18	1
4	12	4	3	-6	-2	15	4	5	-3	-8	1	5	24	1	6	2	5	25	1	0	4	5	29	1
5	12	4	10	2	-1	15	4	23	1	-7	1	5	11	1	7	2	5	18	1	1	4	5	70	1
6	12	4	8	2	0	15	4	9	2	-6	1	5	75	1	8	2	5	15	1	2	4	5	14	1
-8	13	4	10	2	1	15	4	6	-3	-5	1	5	38	1	-11	3	5	3	-6	3	4	5	4	-3
-7	13	4	11	2	2	15	4	4	-4	-4	1	5	71	1	-10	3	5	6	-3	4	4	5	9	2
-6	13	4	5	-3	3	15	4	7	3	-3	1	5	51	1	-9	3	5	3	-6	5	4	5	15	1
-5	13	4	7	2	4	15	4	3	-6	-2	1	5	49	1	-8	3	5	4	-4	6	4	5	37	1
-4	13	4	6	-3	-5	16	4	17	1	-1	1	5	50	1	-7	3	5	13	1	7	4	5	13	1
-3	13	4	24	1	-4	16	4	11	2	0	1	5	5	2	-6	3	5	2	-5	8	4	5	10	2
-2	13	4	8	2	-3	16	4	5	-4	1	1	5	32	1	-5	3	5	52	1	-11	5	5	17	1
-1	13	4	13	1	-2	16	4	5	-3	2	1	5	2	-5	-4	3	5	46	1	-10	5	5	5	-4
0	13	4	14	1	-1	16	4	3	-6	3	1	5	24	1	-3	3	5	107	1	-9	5	5	13	1
1	13	4	3	-6	0	16	4	3	-6	4	1	5	103	1	-2	3	5	15	1	-8	5	5	10	2
2	13	4	10	2	1	16	4	9	2	5	1	5	18	1	-1	3	5	23	1	-7	5	5	9	2
3	13	4	7	2	2	16	4	3	-6	6	1	5	3	-5	0	3	5	23	1	-6	5	5	58	1

Table 21. (Continued)

F(obs) and sigma(F) (-sigma = unobserved): Trichlorobenzene Thiourea Adduct

h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s	h	k	l	Fo	s
-5	5	5	35	1	-10	7	5	8	2	5	8	5	11	2	4	10	5	4	-4	-7	13	5	3	-6
-4	5	5	33	1	-9	7	5	11	2	6	8	5	24	1	5	10	5	9	2	-6	13	5	11	2
-3	5	5	74	1	-8	7	5	3	-5	7	8	5	9	2	6	10	5	26	1	-5	13	5	9	2
-2	5	5	29	1	-7	7	5	25	1	-10	9	5	3	-6	-9	11	5	5	-4	-4	13	5	13	1
-1	5	5	26	1	-6	7	5	3	-5	-9	9	5	3	-6	-8	11	5	3	-6	-3	13	5	3	-6
0	5	5	9	1	-5	7	5	11	1	-8	9	5	13	1	-7	11	5	8	2	-2	13	5	11	2
1	5	5	9	1	-4	7	5	49	1	-7	9	5	7	2	-6	11	5	3	-6	-1	13	5	8	2
2	5	5	22	1	-3	7	5	12	1	-6	9	5	33	1	-5	11	5	16	1	0	13	5	3	-6
3	5	5	28	1	-2	7	5	23	1	-5	9	5	38	1	-4	11	5	27	1	1	13	5	3	-6
4	5	5	53	1	-1	7	5	33	1	-4	9	5	74	1	-3	11	5	14	1	2	13	5	16	1
5	5	5	3	-5	0	7	5	53	1	-3	9	5	3	-5	-2	11	5	11	1	3	13	5	12	2
6	5	5	32	1	1	7	5	13	1	-2	9	5	7	2	-1	11	5	13	1	4	13	5	16	1
7	5	5	5	-4	2	7	5	9	2	-1	9	5	3	-5	0	11	5	10	2	5	13	5	3	-6
8	5	5	3	-6	3	7	5	48	1	0	9	5	11	1	1	11	5	3	-5	-7	14	5	3	-6
-10	6	5	11	2	4	7	5	21	1	1	9	5	7	2	2	11	5	14	1	-6	14	5	4	-4
-9	6	5	3	-6	5	7	5	9	2	2	9	5	48	1	3	11	5	31	1	-5	14	5	7	3
-8	6	5	7	2	6	7	5	5	-4	3	9	5	14	1	4	11	5	7	2	-4	14	5	7	2
-7	6	5	27	1	7	7	5	6	-3	4	9	5	3	-5	5	11	5	3	-6	-3	14	5	6	-3
-6	6	5	25	1	10	7	5	3	-7	5	9	5	10	2	6	11	5	7	3	-2	14	5	13	1
-5	6	5	2	-5	-10	8	5	6	-3	6	9	5	22	1	-8	12	5	3	-6	-1	14	5	12	1
-4	6	5	61	1	-9	8	5	9	2	7	9	5	9	2	-7	12	5	13	1	0	14	5	6	-3
-3	6	5	25	1	-8	8	5	14	1	-9	10	5	14	1	-6	12	5	3	-6	1	14	5	14	1
-2	6	5	33	1	-7	8	5	3	-5	-8	10	5	21	1	-5	12	5	13	1	2	14	5	3	-6
-1	6	5	109	1	-6	8	5	12	1	-7	10	5	16	1	-4	12	5	3	-6	3	14	5	6	-3
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