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

Abstract:
Thiourea's unusual ability to form adducts with hydrocarbons shows promise as a method of separating hydrocarbon mixtures. In an attempt to better understand the forces which hold thiourea adducts together, the crystal structure of two thiourea adducts were determined by x-ray crystallography A diffractometer data set was collected on a crystal of the thiourea adduct with cis para-menthane. This structure was solved in the space group R3bar in a hexangol unit cell with parameters of a=b=15.935(2), c=12.489(2), $\alpha=\beta=90.0°$ and $\gamma=120.0°$. The disorder of the cis para-menthane molecule was successfully modeled and refinement gave a R value of 0.0670.

Another diffractometer data set was collected on a crystal of the thiourea adduct containing a 50 mole percent mixture of 1,2,4 trimethylbenzene and , 1,2,4 trichlorobenzene. This aromatic-thiourea adduct was solved in the space group P2,/c in a monoclinic unit cell with parameters of a=9.886(7), b=15.245(8), c=12.313(6), α=&gamma:=90. O° , and β=112.48° (4). The aromatic molecules in this adduct are disordered and no model was found for them.

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

THE X-RAY CRYSTALLOGRAPHIC DETERMINATION OF THE STRUCTURES

OF THE CIS PARA-MENTHANE THIOUREA ADDUCT AND 1,2,4 TRI-

CHLOROBENZENE-1,2,4 TRIMETHYLBENZENE THIOUREA ADDUCT

by

Mark John Spinti

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of a thesis submitted by

Mark John Spinti

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committee and has been found to be satisfactory regarding
content, English usage, format, citations, bibliographic
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ABSTRACT

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

A diffractometer data set was collected on a crystal of the thiourea adduct with cis para-menthane. This structure was solved in the space group R3bar in a hexangol unit cell with parameters of a=b=15.935(2), c=12.489(2), $\alpha=\beta=90.0°$ and $\gamma=120.0°$. The disorder of the cis para-menthane molecule was successfully modeled and refinement gave a R value of 0.0670.

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

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

INTRODUCTION

Background

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

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

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

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

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

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

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

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

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

Related Research

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

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

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

Table 1

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

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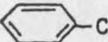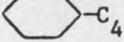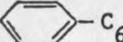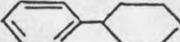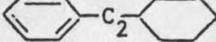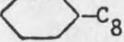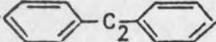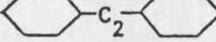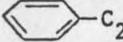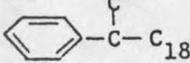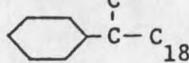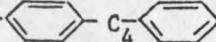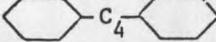
involve hydrogen atoms (8). These distances are-- 3.394A, 3.526A, 3.696A.

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

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

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

Thiourea adducts with non-aromatic hydrocarbons show a structure similar to that of urea adducts. The thiourea molecules form a rhombohedral unit cell, with a pseudo-hexagonal cell similar to that of urea adducts. The space group is R3bar 2/C, with hexagonal axis of a=b= 15.8 A, c=12.5 A and eighteen thiourea molecules per unit cell (1). The c-axis roughly parallels the channel. As in urea adducts, the thiourea molecules form the honeycomb-shaped walls of the channel.

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

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

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

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

molecules thiourea / molecule guest

length of guest molecule

- Cyclopentane
- Pinacolone
- Tetrahydrodicyclopentadiene
- Decalin
- p-Menthane
- Cyclohexylbenzene
- Dicyclohexylamine
- p-Dicyclohexylbenzene
- Dihydrocitronellyl pivalate
- Citronellyl isovalerate

Table 2

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

9
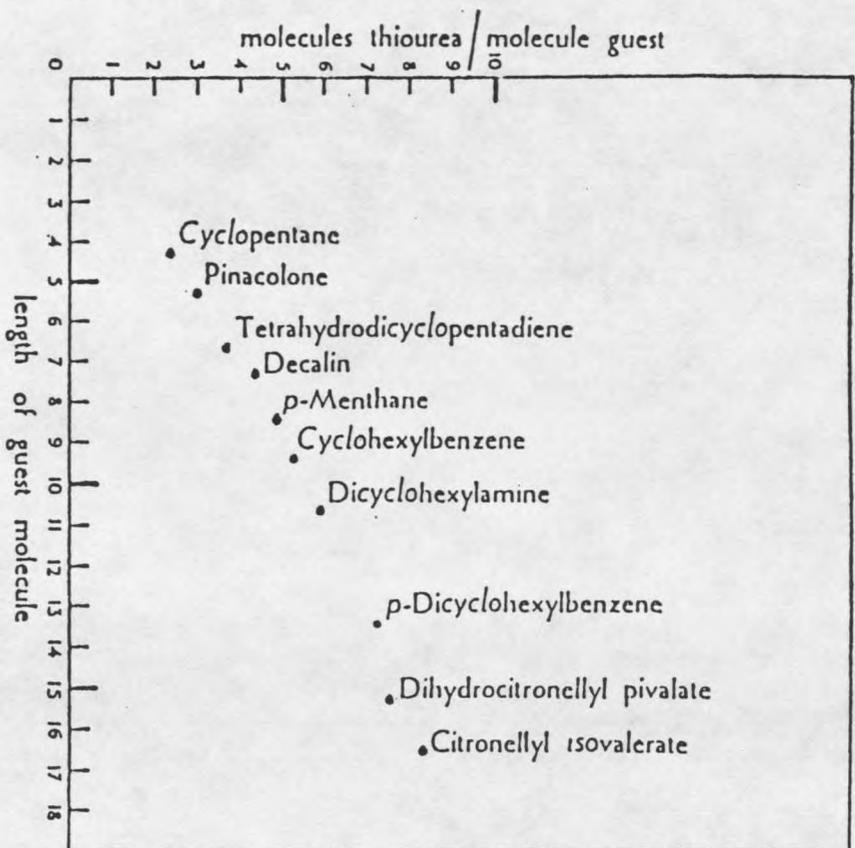
The differences in the arrangement of the urea and thiourea molecules in their respective adducts can be seen in Figure 1. The arrows point from the oxygen or sulfur atom to the carbon atom of the urea or thiourea molecule. From the thiourea adduct structures Schlenk found that three sulfur atoms are coplanar (4). The sulfur atoms point straight into the center of the channel. These planes are 12.5A apart in the c direction; this is the unit cell dimension along the c-axis. Figure 1 shows these planes as hatched areas.

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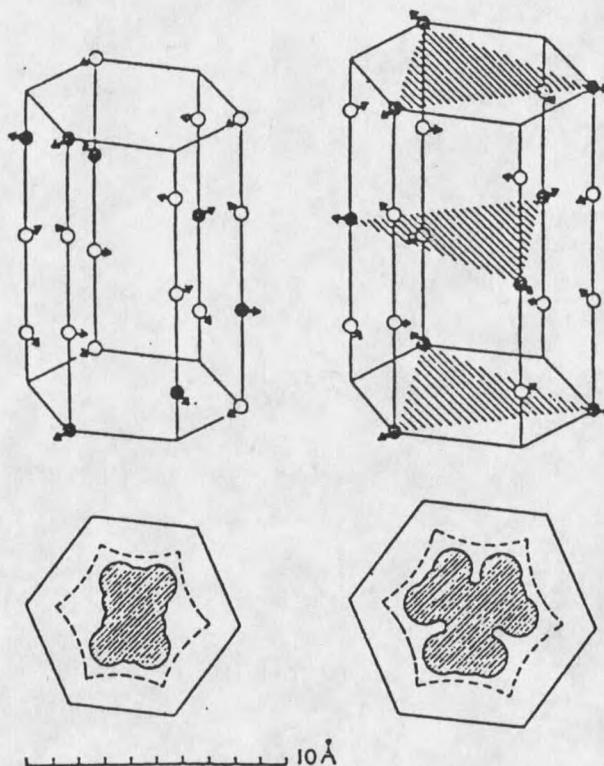
Figure 1

Lattice of urea (left) and thiourea (right) adducts
Top: Each circle represents a urea or thiourea
         molecule, the arrrow points from the
         oxygen or sulfur atom towards the carbon
         atom. The filled circles represent a
         spiral of urea molecules in the urea
         lattice and the coplanar sulfur atoms in
         the thiourea lattice.
Bottom: cross section with included hydrocarbons
     [reproduced from Schlenk (4)]

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

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

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

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

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

Table 3

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

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

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

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

Welling suggested some possible explanations of the action of adductors and non-adductors based on the electron configuration of the molecules (3). As mentioned earlier, benzene will not adduct with thiourea, but the isomers of TCB will. Therefore, the size or planar nature of the benzene molecule can not be responsible for inhibiting the formation of an adduct. In thiourea both the sulfur and nitrogen atoms have lone pairs of electrons. The electronic structure of benzene contains pi clouds which lie above and below the plane of the carbon atoms. These pi electrons are delocalized and form a "donut" of electron density. Welling suggested that the repulsion forces between the pi electrons of benzene and the lone pairs of electrons in nitrogen and sulfur are too great to allow the formation of the thiourea lattice. The chlorines of TCB must somehow influence the formation of the adduct. Welling asserted that the chlorine atoms are involved in hydrogen bonding.
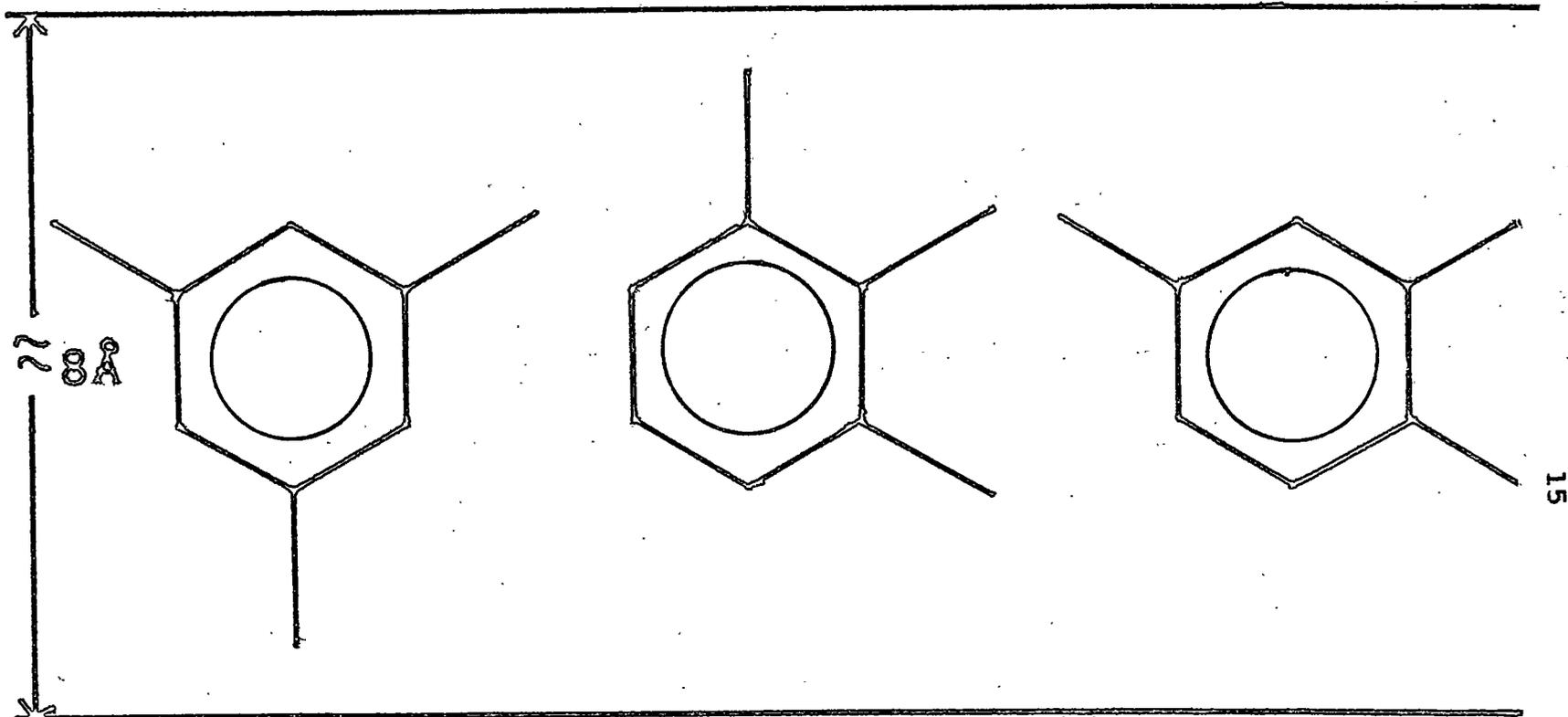
Figure 2

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

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

In related work Fait and Fitzgerald (14) determined
the crystal structures for the cyclohexane-thiourea adduct
and the carbon tetrachloride-thiourea adduct. The unit cell
parameters reported for these structures are presented in
Table 4. Both of these structures are in the space group
R3bar, which is typical of non-aromatic adducts, and
exhibit the honey-comb type channel structure formed from
thiourea with the adduct molecule occupying the channel.
The channel structure is illustrated in Figure 3 which is a
stereoview of the carbon tetrachloride structure looking
down the c-axis.

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

Table 4

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

Hydrocarbon Adducted with	A	B	C	α	β	γ	Space Group
Cyclohexane	15.708(1)	15.708(1)	12.431(2)	90.0	90.0	120.0	R3bar
CCl_4	15.539(1)	15.539(1)	12.529(2)	90.0	90.0	120.0	R3bar
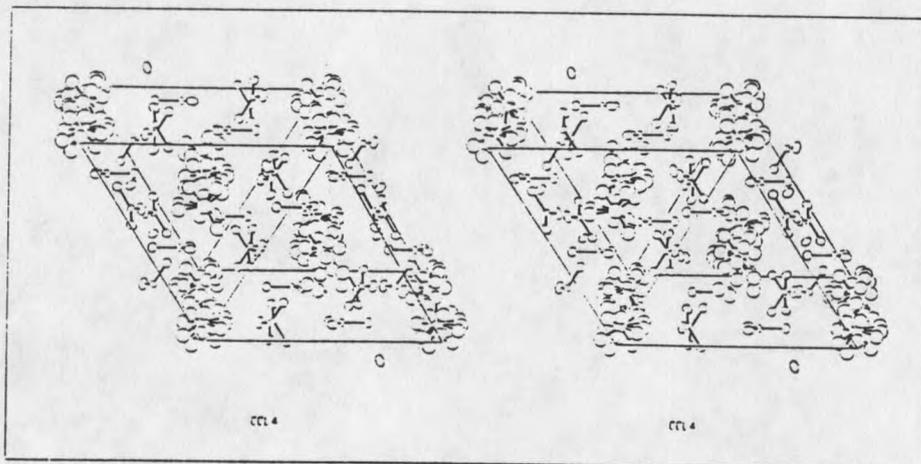
Figure 3

Stereoview of carbon tetrachloride-thiourea adduct
viewed down the channel, offset by 20° and
showing the disorder of the carbon
tetrachloride molecule.
[from Fait and Fitzgerald (14)]

Table 5

Cyclohexane-thiourea adduct sulfur-aromatic carbon
distances. [from Fait and Fitzgerald (14)]

Atom 1	Atom 2	Distance
S1	C13	3.7918A
S1	C12	3.8306A
S1	C14	3.8697A
S1	C11	3.9577A

Table 6

Carbon tetrachloride-thiourea adduct sulfur-chlorine
distances [from Fait and Fitzgerald (14)]

Atom 1	Atom 2	Distance
S1	CL5	3.5831A
S1	CL3	3.7588A
S1	CL2	3.9808A
S1	CL1	3.9856A

channel molecules for each of these structures. This same arrangement is seen in all of the thiourea adduct walls. From these distances and spacial oreintations, Fait and Fitzgerald suggest that there is an interaction between the thiourea sulfur atom and atoms of the enclosed molecule.

Also in related work Wick and Fitzgerald determined the crystal structure of 1,2,4 TCB (15). This structure is in the space group $P2_1/c$, which is the same as the aromatic structures reported by Welling (3). Table 7 contains structural information for this structure. The channel walls of this structure are similar to the wall structure seen in the non-aromatic structures, except that the walls are no longer hexagonal. The channel has been distorted to allow the bulkier aromatic molecule to fit in. This shows the flexibility of the thiourea channel structure to change its shape under the influence of the guest molecule.

An interesting characteristic of thiourea is its selectivity for some geometric-isomers. Thiourea will selectively form an adduct with cis-para menthane (1-isopropyl, 4-methyl cyclohexane) over trans-para menthane (5).

Table 7

Structural parameters for 1,2,4 TCB-thiourea adduct
structure [from Wick and Fitzgerald (15)]

Hydrocarbon Adducted with	A	B	C	α	β	γ	Space Group
1,2,4 TCB	9.779(1)	15.355(1)	12.293(2)	90.0	111.85	90.0	$P2_1/c$

Research Objectives

The objective of this research was to determine crystal structures of thiourea adducts which would help to explain the behavior of thiourea adducts. This would be accomplished by:

1) Determination of the crystal structure of the 1,2,4 TCB-1,2,4 TMB thiourea adduct and comparison to the structures found by Welling (3), Fait and Fitzgerald (14), and Wick and Fitzgerald (15).

2) Obtaining an adduct structure in which the hydrocarbon is sterically hindered enough to allow use of a model for the hydrocarbon molecule in the channel with minimal disorder.

3) From the adduct structures determination of the characteristics of the interaction between the thiourea molecules and the hydrocarbon molecules.

EXPERIMENTAL

Crystal Growth

Obtaining crystals satisfactory for x-ray diffraction proved difficult. The quality and size of crystals obtained depended on the thiourea and hydrocarbon concentrations, and on the rate of cooling. Each hydrocarbon investigated behaved differently when forming adducts. In all cases methanol was saturated with thiourea by heating a mixture of methanol and solid thiourea. Then the hydrocarbon was added. After stirring, the mixture was heated to dissolve any adduct that formed. When the mixture cleared, it was removed from the heat and sealed. The mixture was allowed to cool to room temperature. The crystals best suited for x-ray diffraction study appeared in 12 to 24 hours.

Adducts form long, clear, hexagonal, needle-like crystals. Pure thiourea crystals are typically clear, hexagonal plates, but also form odd shapes crystals. These are sometimes difficult to tell apart from short adduct crystals.

1,2,4 TMB and 1,2,4 TCB adduct

A 50-50 weight percent mixture of 1,2,4 TMB and 1,2,4 TCB was prepared. About 5 milliliters of this mixture was added to 20 milliliters of methanol saturated with thiourea. This procedure gave crystals of satisfactory quality.

Cis para-menthane adduct

Three milliters of cis para-menthane were added to 20 milliters of methanol saturated with thiourea. These crystals were of better quality than the aromatic adducts.

Crystal Analysis

Crystals containing a mixture of hydrocarbons were analyzed using a Varian Aerograph Series 1400 Gas Chromatograph with strip chart recorder. A batch of crystals to be analyzed was vacuum filtered from the mother liquor and then spread out on paper towels to air dry. Prolonged exposure to air causes most adduct crystals to deteriorate and become an opaque white color. After drying for a couple of hours, the crystals were dissolved in a minimum amount of boiling water. When all the crystals were dissolved the solution was allowed to cool and two phases formed. The organic phase was separated from the aqueous

phase in a separatory funnel. A sample of the organic phase was then analyzed using the gas chromatograph. Helium was used as the carrier gas.

A 5% diisodecylphthalate and 5% bentone 34 on Chromasorb W column at 150° C was used to analyze the aromatic mixtures. Known samples were used to find the relationship between area percent and mole percent. From known samples of 1,2,4 TMB and 1,2,4 TCB solutions it was determined that for these compounds area percent exactly corresponds to mole percent.

A method for analyzing the hydrocarbons in a single adduct crystal was developed. A single crystal was placed in a minimum amount of solvent (2 ml of acetone, aceto-nitrile or a heavy alcohol) and allowed to dissolve for an hour. A sample of this solution was then analyzed using the gas chromatograph. The best solvent to use depends on the gas chromatograph column used and for what hydrocarbons the analysis is being done to detect. A solvent that forms a single phase when the adduct is dissolved and does not interfere with the hydrocarbon peaks on the strip chart is desired.

Adduct Density

A floation method was used to determine the density of adducts. Adducts were suspended in a mixture of two miscible liquids, one more dense than the adduct and one less dense. A mixture of carbon tetrachloride and methanol was used to suspend adducts. When a mixture which would just suspend an adduct, that is the adduct would neither sink nor float, was obtained, 10 ml of the solution was removed and weighed and the density calculated.

Crystal Mounting

Crystals were removed from the mother liquor and placed in a drop of Paratone-N on a microscope slide. Under the microscope the crystals were cut across their length. It was difficult to get a clean cut on the adduct crystals, as they often fractured along their length. Some crystals resembled a bundle of smaller needle-like crystals, a few were even hollow tubes. Pieces of crystals that were of the right size, shape and showed no signs of twinning (multiple crystal growth) were checked to see if they extinguished under polarized light. Those that did extinguish, indicating a single crystal, were selected for mounting.

To prevent deterioration, crystals were mounted in sealed glass capillary tubes. The cis-para menthane-

thiourea crystal used for data collection was cylindrical
with a diameter of 0.8 millimeters and a length of 1.2 mm.
The 1,2,4 TMB-1,2,4 TCB adduct that was used for data
collection was also cylindrical with a diameter of 0.7
millimeters and a length of 0.8 mm. It was found that a
larger crystal, such as those used, were desired in order
to give observable reflections out to larger angles, since
the disorder within the crystal made the high angle
reflections weak.

Photographic Film Studies

Weissenburg photographs were collected and used to
select satisfactory crystals. Once a satisfactory crystal
was found, oscillation, zero level, first level and second
level Weissenberg photographs were taken. Copper radiation
with a nickel filter was used to take the Weissenburg
photographs. These photographs were used to determine
crystal quality and to estimate unit cell parameters.

Diffractometer Data Collection

Intensity data for both compounds were collected on a
Nicolet R3mE four circle diffractometer using the ω scan
technique, with MoK_2 radiation monochromated with a
graphite crystal monochromator. Both data sets were

collected at room temperature. In each case three standard reflections were collected every one hundred reflections throughout the course of the data collection. There was no decrease in these standards over the course of the data collection on either crystal. Data for the cis-para menthane adduct was collected on the hexagonal unit cell. Data was collected on both crystals from 3° to 50° on 2Θ. Only unique reflections in the sphere were collected. Lattice parameters for both crystals were obtained from a least-squares fit of 25 centered reflections which were selected from the data set and then recollected. These 25 centering reflections for the 1,2,4 TCB-1,2,4 TMB adduct were in the range 22°<2Θ<28°. The 25 centering reflections for the cis-para menthane adduct were in the range 27°<2Θ<34°. Asmuithal adsorption correction data was collected for both structures, but the transmittance varied so little that no correction was necessary. The linear absorption factors used were: for the 1,2,4 TMB-1,2,4 TCB adduct $\mu(MoK_2)$= 6.53 cm^{-1}, for the cis para-menthane adduct $\mu(MoK_2)$= 3.95 cm^{-1}.

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 anomalous scattering terms for all types except H were taken from

International Tables for X-ray Crystallography (16); all atoms were assumed to be in the zero ionization state. The 1,2,4 TCB-1,2,4 TMB structure was solved initially by direct methods. Since the thiourea molecules in the cis-para menthane structure are isostructural with the thiourea molecules in the cylcohexane structure found by Fait and Fitzgerald (14), sulfur positions from the carbon tetrachloride structure were used for initial phasing of the cis-para menthane structure. Both of these stuctures were refined using a blocked cascade least-squares refinement program in which the minimized function is:

$$M = \Sigma \text{Weight}(|F_{obs}| - |F_{calc}|)^2 \quad (17),$$

in which Weight is a weighting factor, F_{obs} is the observed structure factor and F_{calc} is the calculated structure factor. The thiourea model in both adducts was well defined, and in the final stages of refinement the thiourea portion of the model was refined anisotropically. The major problem with both of these structures was with generating a model which described the disorder of the hydrocarbon in the channel. As the model improved the hydrogen atoms of the thiourea molecules began appearing in the difference maps and were added to the structure.

RESULTS AND DISCUSSION

Discussion of X-ray Crystallography

When x-rays pass through a crystal they are diffracted
by the electrons of the atoms in the crystal, creating a
diffraction pattern. This diffraction occurs in accordance
with Bragg's Law ($n\lambda = 2d \sin\Theta$ where $\lambda =$ wavelength of
incident radiation, d=distance between reflecting planes,
$\Theta =$ angle between the incident or reflected radiation and
the reflecting surface, m=1,2,3,...). The positions and
intensities of these diffracted x-rays are recorded. A
diffractometer collects this information with a radiation
counter which gives accurate intensity measurements. The
intensity of a diffracted x-ray is determined by the
positions and scattering factor (related to the atomic
number) of the atoms in the crystal. The angles at which
the diffraction occurs depends upon the lattice parameters
of the crystal. Thus, the intensities of the diffracted x-
rays depend on this structure. Information about the phases
of the diffracted x-rays is not directly observable in the
diffraction pattern. The solution of a crystal structure
involves the development of sufficient phase information so
that an adequate model for the arrangement of the atoms in

the crystal can be obtained which refines to produce agreement between observed and calculated structure factors. Initial models can be extended using Fourier syntheses and refined by least squares procedures. The lengthy calculations involved are made possible by use of computers.

The systematic absences of reflections (extinctions) are determined by space group symmetry. Thus observation of systematic absence reflections allows determination of the symmetry of the crystal. However, the space group may not be uniquely defined by the systematic extinctions.

The probable correctness of a model can be measured by the R value. The R value measures the agreement between observed and calculated structure factors: different methods of weighting the structure factors give different R values. One R value is given by the equation:

$$R = \frac{\Sigma ||F_O|-|F_C||}{\Sigma |F_O|} \, ,$$

other R's are:

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

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

$$R_m = R_g \text{(calculated for the scale factor which minimizes } R_g),$$

where $|F_O|$ is the scaled observed structure factor and $|F_C|$ is the calculated structure factor (17). A further

explanation of x-ray crystallography can be found in Stout and Jensen (18).

Cis para-Menthane-Thiourea Adduct

As mentioned earlier thiourea selectively forms adducts with cis para-menthane (1-isopropyl, 4-methylcyclohexane) over trans para-menthane (5). This selectivity for a geometric isomer prompted further study. It was found that cis para-menthane easily forms crystalline adducts that are of fairly good quality for x-ray diffraction study.

The crystal density determined by floation was 1.16 g/ml. From this value the mole ratio of thioureas to cis para-menthanes was calculated to be 4.62. This is consistent with the value of about 4.8 obtained from Schlenk's graph (Table 2).

A diffractometer data set was collected on a cis para-menthane-thiourea adduct. This data set contained 3480 intensities, of which 969 were considered observed reflections.

Laue group symmetry suggested a space group of R3bar. A least squares fit of 25 selected reflections gave unit cell parameters of a=b=15.935(2)A, c=12.489(2)A , $\alpha=\beta=90.0°$ and $\gamma=120.0°$ (numbers in parentheses are standard deviations).

Indications of a super-lattice were seen in the axial photographs taken on the diffractometer prior to data collection. The axial photographs taken on rhombohedral axis contained spots that do not line up with the other layer lines. These fourteen reflections in between layer lines were seen on all three rhombohedral axial photographs and were about one-third of the distance in between layer lines. These indications prompted the collection of a thin shell of $2\Theta=3.0°$ to $2\Theta=12.0°$ with hk21 and then 2h2kl. No indications of a super-lattice were seen in these data sets. In retrospect it might have been best to collect a thin shell with hk31.

After initial phasing with the sulfur position from the isostructural carbon tetrachloride adduct (14), the thiourea molecules were easily located on difference maps. At first any peaks that showed up in the channel were added to the model and were allowed to refine. This procedure gave a solution with a low R value (R=0.0427), but the carbon atoms in the channel made no chemical sense. In the search for a cis para-menthane molecule in the channel it was noticed that if the channel were viewed down the c-axis a repeating pattern could be seen.

As Figure 4 shows, the atoms in the channel appear to form a small circle ringed by a larger circle. The 3-fold
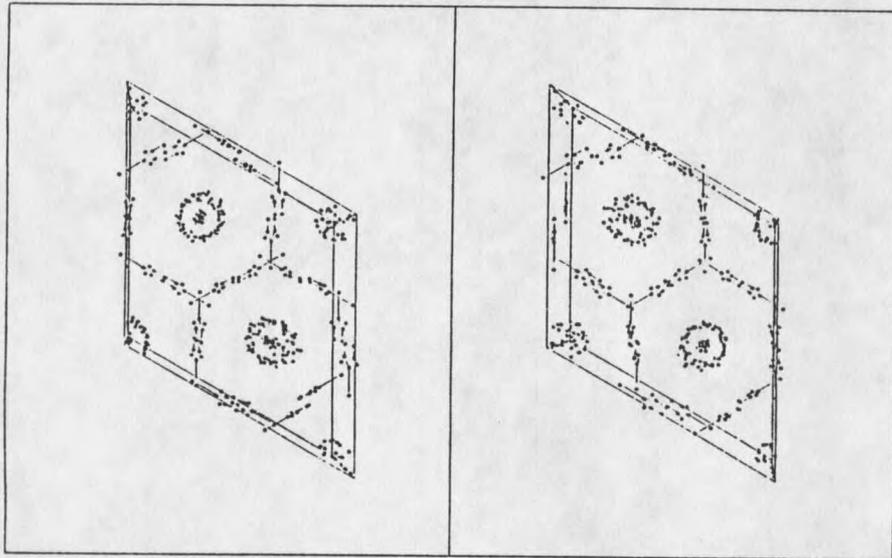
Figure 4

Cis para-menthane adduct without the model for the
hydrocarbon molecule, viewed down the c-axis

axis of symmetry runs down the middle of the channel in the c-direction. This suggests that some of the atoms of the cis para-menthane molecule lie on or near the 3-fold axis and the others are located on the larger circle. If this were the case, it would appear that the cis para-menthane molecule is disordered because it is free to orientate itself about the 3-fold axis in the channel. From the 19 carbon atoms in the channel· ten that roughly formed a cis para-menthane molecule were found and then constrained to form an idealized cis para-menthane molecule. In the final stages of refinement a weighting factor was used. The weighting factor was Weight=1/(.sigma**2(F)+G*F*F) where G=0.00040. Refinement of this model gave a reasonable R value (R=0.0670, R_w=0.0707, R_g=0.0986, R_m=0.0986, goodness of fit=3.341). This model was used to find interatomic distances which would characterize the interactions between the thiourea sulfur atom and the cis para-menthane molecule. Appendix B contains tables for publication for this structure.

Figure 5 shows the constrained cis para-menthane molecule. Figure 6 also shows the constrained cis para-menthane molecule but is a space filling plot with four generated hydrogens. The cis para-menthane molecule is disordered about the three fold axis, which runs parallel to the center of the channel, with three equivalent

Figure 5

Constrained cis para-menthane molecule with 50%
probability ellipsoids
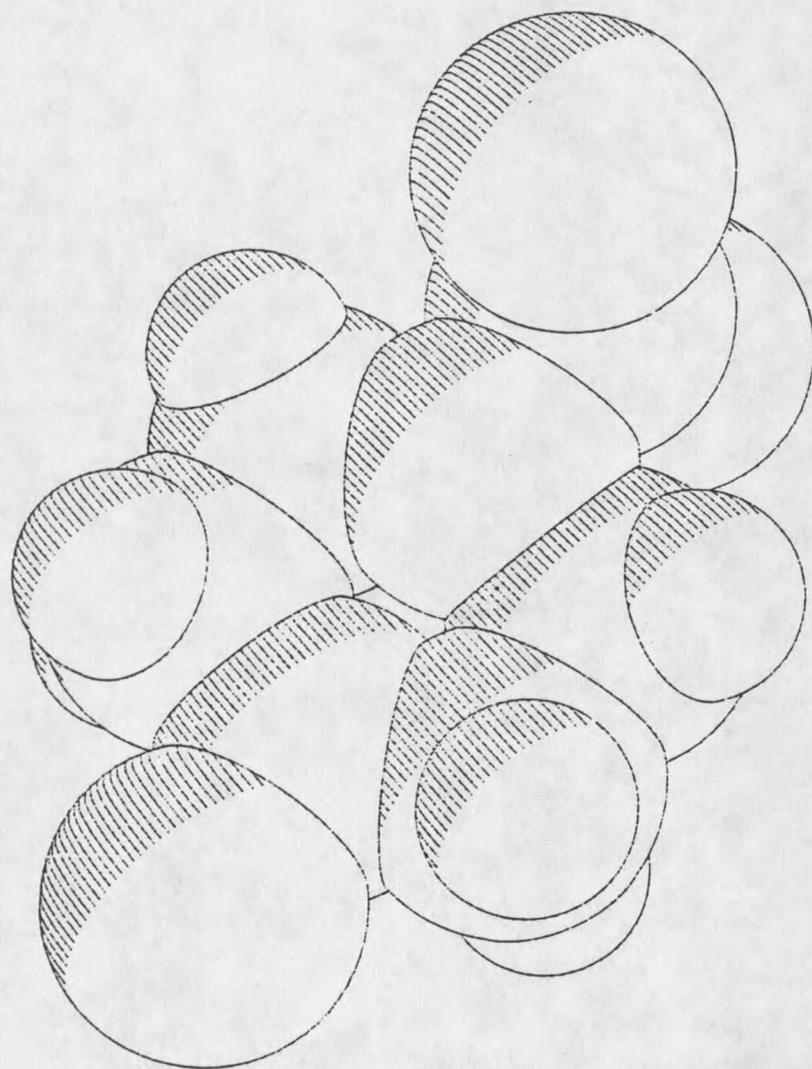
Figure 6

Space-filling plot of constrained cis para-menthane
molecule
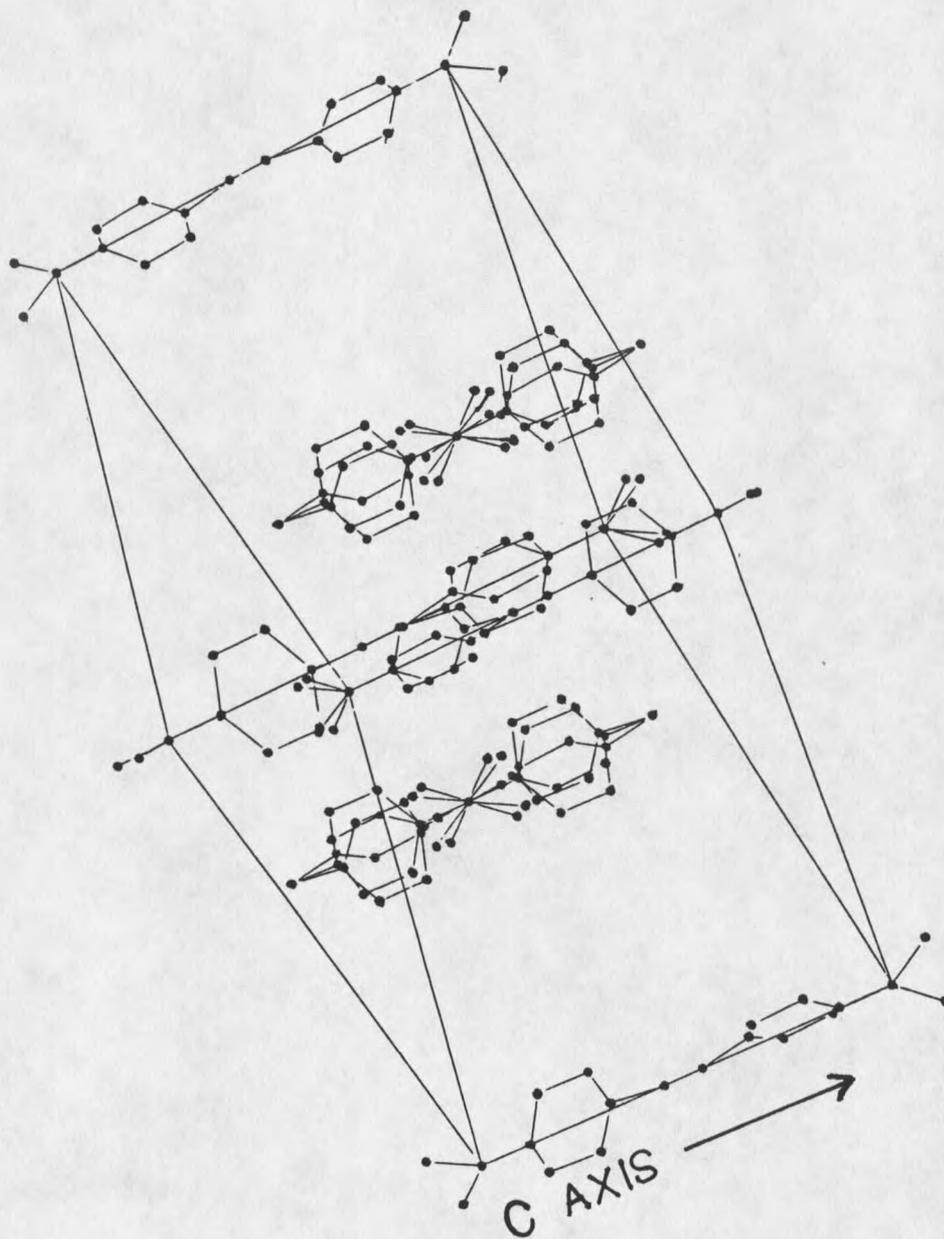
Figure 7

Packing plot of cis para-menthane molecule showings it's
three orientations about the three fold center
of symmetry

positions 120° apart. This disorder can be seen in Figure 7 which contains only the cis para-menthane molecule.

Interatomic distances between non-bonded atoms were calculated using the graphics package in SHELXTL program package (17) and from the XTAL system of crystallographic programs (19).

Figure 8 shows a single sulfur atom hydrogen bonded to four other thiourea molecules (the open lines are hydrogen bonds). These hydrogen bonds are of four lengths: 3.4022(0.0096)A, 3.4054(0.0043)A, 3.4375(0.0040)A and 3.4579(0.0058)A (numbers in parentheses are standard deviations). Figure 9 is a stereo view looking down the channel offset by 20°; in the plot some of the hydrogen bonds are drawn in as dotted lines. All of these bonds lengths are longer than the shortest hydrogen bond in crystalline thiourea at room temperature which is 3.394A (8), although the difference between 3.4022A, 3.4054A and 3.394A may not be significant. The four hydrogen bond lengths in the thiourea network of the adduct are all significantly shorter than the remaining two hydrogen bond lengths in crystalline thiourea at room temperature, 3.526A and 3.696A (8).

These shorter hydrogen bonds indicate that the thioureas are more closely packed in the walls of the
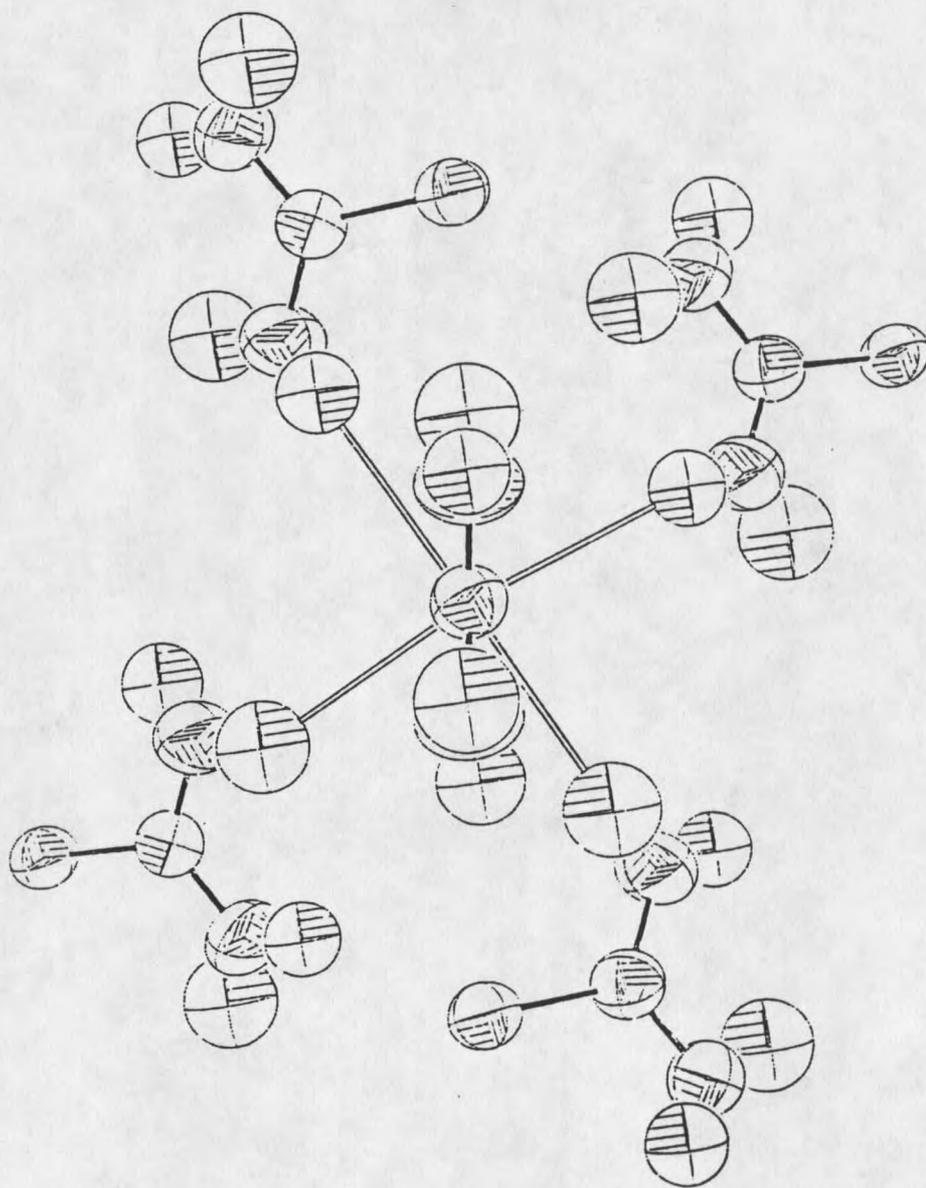
Figure 8

Hydrogen bonding scheme in the thiourea network of the
cis para-menthane adduct viewed down the sulfur-carbon
bond of a thiourea molecule. The open lines are
hydrogen bonds.
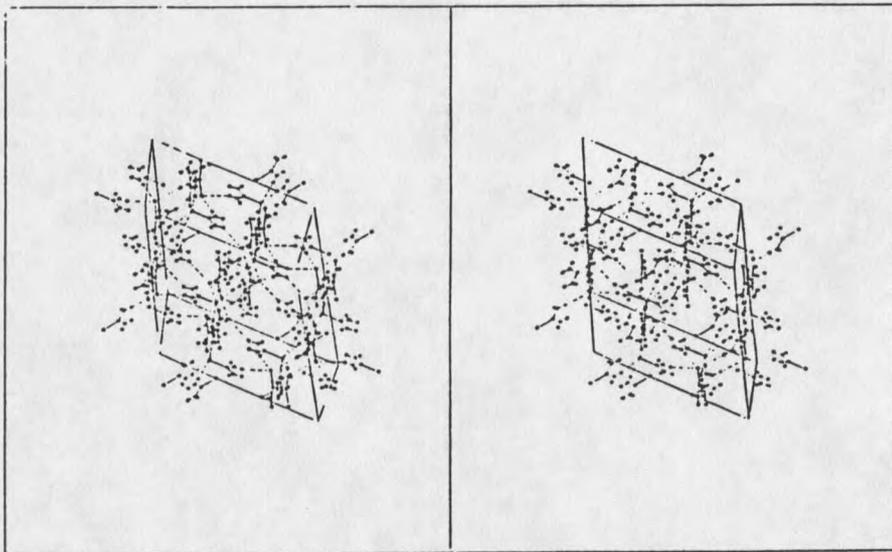
Figure 9

Stereoview of the hydrogen bonding in the thiourea
network of the cis para-menthane adduct
structure, viewed down the c-axis
offset by 20°. Some hydrogen
bonds are drawn in
as dotted lines.

adducts than in crystalline thiourea at room temperature. As Fetterly pointed out in his study of urea adducts, the tighter packing and shorter hydrogen bond lengths indicate a lower energy state. These strong hydrogen bonds contribute to the formation of the adducts, but contrary to Fetterly's opinion they by themselves probably do not hold the adducts together. This is evident from the fact that some hydrocarbons form adducts while other hydrocarbons of the same geometry will not form adducts. An example of this is cyclohexane which will form an adduct and benzene which will not form an adduct (see Table 1). Another strong indication of an interaction between the hydrocarbon molecule and the thiourea's sulfur atom is that adducts vary so widely in stability. Most adducts are unstable in air, but the adduct containing bicyclo[2.2.2] octane is stable in air (14).

Schlenk found that in the thiourea network there occurs three coplanar sulfur atoms every unit cell length in the c-direction (12.5A), and all three of these sulfurs are pointing into the center of the channel (4). This pattern was found in the cis para-menthane adduct. The relationship between the sulfur atoms and the hydrocarbon molecules can be seen in Figure 10. The three planar sulfur can be seen pointing in at the cyclohexane ring of the cis para-menthane. Figure 11 shows three thiourea molecules
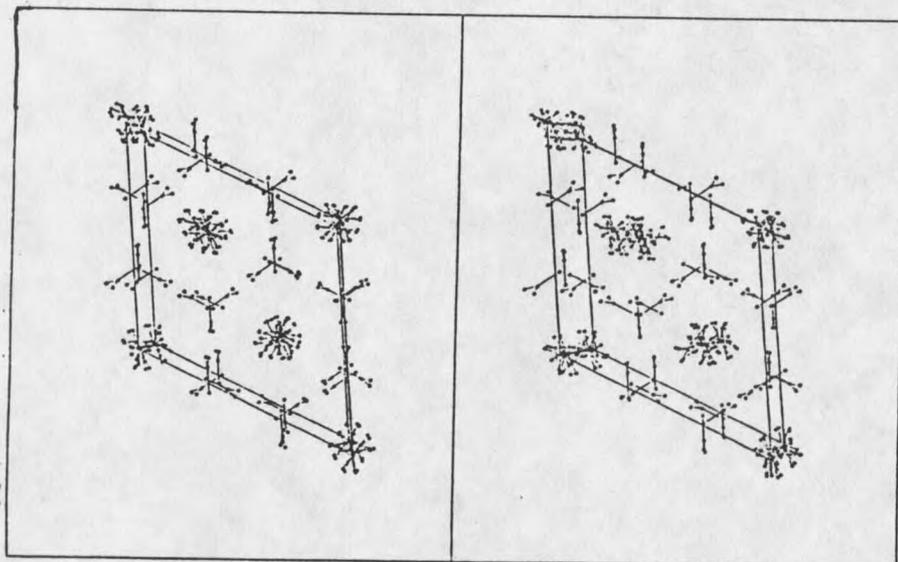
Figure 10

Stereoview of the cis para-menthane adduct structure
with a model for the cis para-menthane molecule,
viewed down the c-axis offset by 20°.
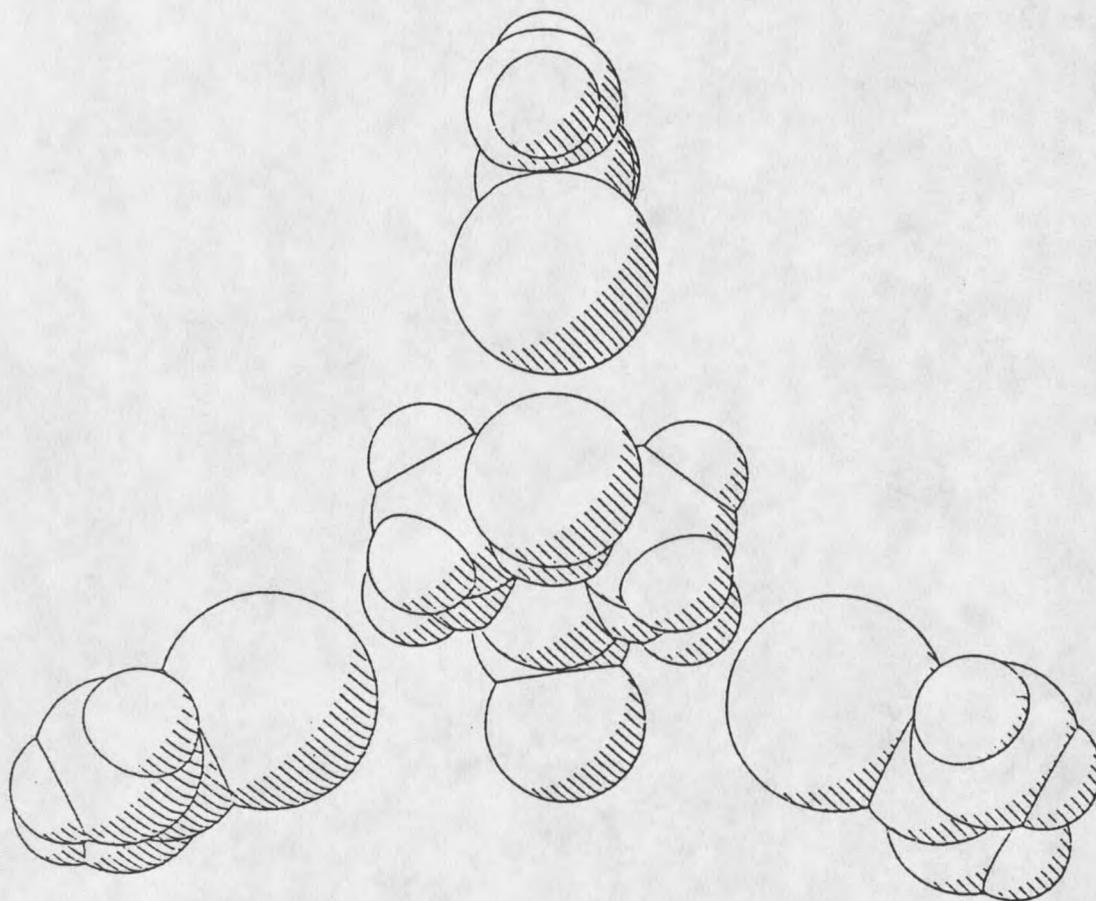
Figure 11

Space-filling plot of three thiourea molecules with planar
sulfur atoms and the cis para-menthane molecule with eight
generated hydrogen atoms viewed down the c-axis

with coplanar sulfur atoms and their position in relation to the cis para-menthane molecule; only one of the three equivalent positions is shown. The orientation of the ring carbons and the sulfur atoms is evident. One of the sulfur atoms is pointing in between the center of the ring while the other two sulfur are pointing in at the two carbons on each side of the ring. This relationship can also be seen in Figure 12 which is a view looking down the sulfur-carbon bond of thiourea molecule which points into the middle of the ring. The distances from each of these sulfur atoms to the ring carbons are in Table 8.

The distances between S1, the sulfur pointing into the center of the cyclohexane ring, and the ring carbons are all too long for a very strong interaction to occur (see Table 8). The other two sulfur atoms, S1A and S1B, and the carbons on the sides of the ring are close enough for an interaction to take place (see Table 8). A hydrogen bond is possible if the atoms are closer than the sum of their van der Waal radii. The van der Waal radius of sulfur is 1.76±0.04A and that for hydrogen is 1.20A (20). The radius for the carbon-hydrogen covalent bond is 1.08A (13). For a hydrogen bond in which the hydrogen atom is linearly in between the carbon and sulfur atom, the shortest non-bonded distance is the sum of these three radii, which is 4.04A.
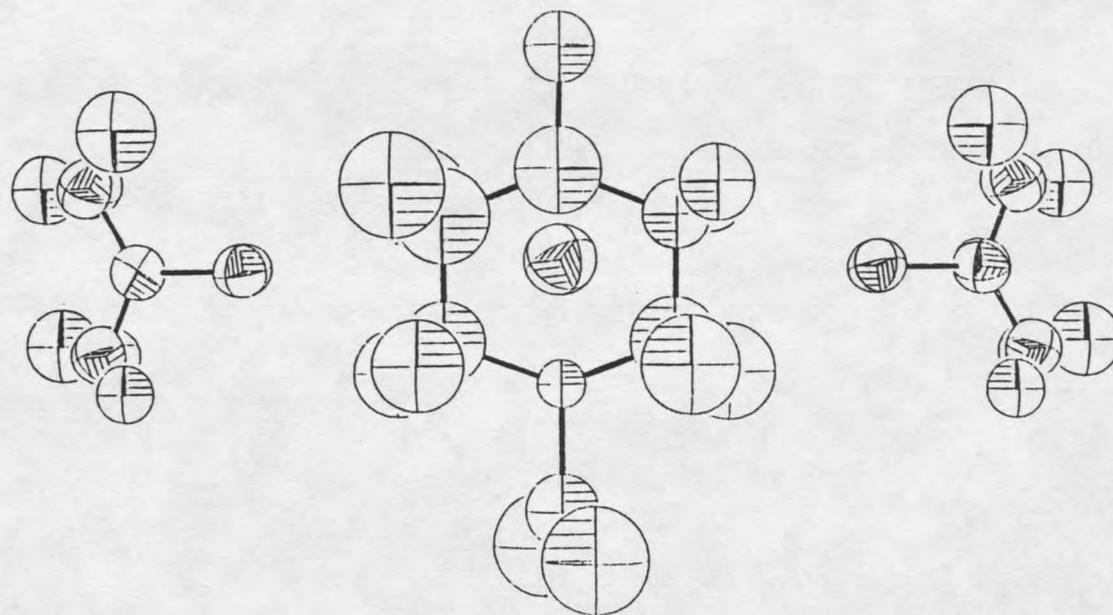
Figure 12

Three thiourea molecules with planar sulfur atoms and a
cis para-menthane molecule with eight generated
hydrogens, viewed down the S-C bond of a
thiourea molecule with the NH_2
group removed

Table 8

Interatomic distances between sulfur and carbon,
or sulfur and hydrogen atoms in the cis para-
menthane adduct structure. Numbers in
parentheses are standard deviations.

Atom 1	Atom 2	Distance (in A)
S1	CR1	4.6946(0.0231)
S1	CR2	4.6392(0.0263)
S1	CR3	4.9911(0.0030)
S1	CR4	4.8403(0.0505)
S1	CR5	4.8973(0.0454)
S1	CR6	4.5926(0.0177)
S1A	CR1	3.9073(0.0279)
S1A	CR2	4.0637(0.0273)
S1A	HR1B	3.105
S1A	HR2A	3.342
S1B	CR5	3.7429(0.0276)
S1B	CR4	3.8925(0.0321)
S1B	HR5A	3.018
S1B	HR4A	3.177

Table 9

Van der Waal radii distances between sulfur and carbon atoms
in the cis para-menthane adduct

Atom 1	Atom 2	Distance (in A)
S1A	CR1	3.87
S1A	CR2	3.78
S1B	CR5	3.79
S1B	CR4	3.78

From the distances in Table 8 it can be seen that S1A and S1B seem to be close enough to the ring carbons to be hydrogen bonded, but the hydrogen atoms are not linearly in between the sulfur atoms and the carbons. All of thehydrogen atoms are more than 2.96A (1.76A+ 1.20A) from the closest sulfur atom.

Since the sulfur, hydrogen and carbon atoms are not linear, they form a triangle. The angles of the triangle and the length of two sides, the van der Waal radii distance between the sulfur and hydrogen and the C-H covalent bond radius, are known. By trigonometry the third side, the sulfur-carbon distance can be found. Table 9 contains the calculated distances between the sulfur and carbon atoms. These values represent the distance at which the sulfur and carbon atoms overlap thier van der Waal radii. The overlapping of van der Waal radii would indicate the beginning of a hydrogen bond. Only S1B and CR5 are closer than this calculated distance.

Only this interatomic distance between S1B and CR5 provides evidence of hydrogen bonding between the sulfur atoms and the cyclohexane ring C-H groups. All of the sulfur atoms are close enough to the C-H groups for some interaction. The most likely form of interaction is a dipole-dipole attraction. The double-bonded sulfur atom has

two unshared pairs of electrons which are on the opposite side of the sulfur atom from the double bond. It is quite possible that these electrons could induce an added dipole in the C-H group. The strength of this interaction contributes to the lowering of the energy state of the adduct.

Figures 7 and 11 provide an insight into why thiourea is selective for cis para-menthane over trans para-menthane. In Figure 11 the methyl group is in the channel, right above the cyclohexane ring. One would expect the trans para-menthane molecule to lie in the same location as the cis para-menthane molecule. Also, the isopropyl group would be in the same position because of its size. This leaves only the methyl group to be positioned differently; it would be forced to stick out above the ring carbon and away from the center of the channel. In this position the trans methyl group would be close to one of the NH_2 groups of a thiourea molecule to which the sulfur atom is hydrogen bonded. This proximity might cause distortion of the molecule that is not present with the cis methyl group and cause the trans para-menthane adduct to be a little higher in energy than the cis para-menthane adduct. This small energy difference could be enough to account for thiourea's selectivity for cis para-menthane.

1,2,4 TMB-1,2,4,TCB-Thiourea Adduct

Gas chromatography analysis of the 1,2,4 TMB and 1,2,4 TCB-thiourea adduct indicated that thiourea is selective for 1,2,4 TCB over 1,2,4 TMB (Table 10). It was found that a feed mixture of 50 weight percent 1,2,4 TMB and 1,2,4 TCB gave crystals which were close to 50 mole percent of each aromatic compound (Table 10).

Table 10

Gas chromatograph analysis of 1,2,4 TMB and 1,2,4 TCB
adduct feed, mother liquor after adduct
formation, and extract

	1,2,4 TMB	1,2,4 TCB
Feed		
wt%	50	50
mole%	60.2	39.8
Mother		
Liquor		
mole%	63.4	36.6
Adduct		
Extract		
mole%	51.3	48.7

The measured density for the 1,2,4 TMB and TCB adduct crystal was 1.28 g/ml. This value is reasonably close to the 1.3 g/ml reported by Welling (3). The mole ratio of thiourea to aromatics was calculated to be 4.43.

A x-ray diffraction data set was collected on a 1,2,4 TMB and 1,2,4 TCB-thiourea adduct which contained 50 mole percent of each aromatic. This data set contained 3462 intensities, of which 1725 were considered to correspond to observed reflections. In these reflections the following extinctions were found:

Table 11

Reflections absent and the symmetry indicated for the 1,2,4 TMB-1,2,4 TCB adduct

Reflections Absent	Symmetry Indicated
U00	
U0G	n glide perpendicular to b
U0U	
0U0	2 fold screw axis on b

A space group of $P2_1/c$ was determined from these extinctions. The unit cell parameters of a=9.886(7)A, b=15.245(8)A, c=12.313(6)A, $\alpha=\gamma=90°$ and $\beta=112.48(4)°$ (numbers in parentheses are standard deviations) were determined from the least squares fit of 25 selected reflections.

The sulfur positions were determined by direct methods. Thiourea carbon and nitrogen atoms showed up in the difference maps. Initially, any peak which showed up in the channel was added to the model, but this failed to

produce any recognizable molecule in the channel and did not significantly lower the R value. First two, then four idealized aromatic rings were constrained. The calculated density was used to find the site occupation factors for these rings. Difference map peaks with the appropriate geometry were constrained as methyl groups or chlorine atoms. Only two peaks that refined as chlorine atoms were found. No model that was tried provided a R value lower than 0.140. The disorder in the channel is so great that almost any reasonable model will account for some of the electron density, but will not provide an accurate enough model to allow determination of interatomic distances with any degree of accuracy. This prevents any conclusions about the interactions between the thiourea molecules and the channel hydrocarbons.

A model with four coplanar idealized benzene rings was used in refinement. These benzene rings were in two pairs, and all four rings were coplanar. The rings in each pair were only shifted slightly from each other. Only two peaks refined as chlorine atoms.

Figure 13 is a stereoview down the channel of the 1,2,4 TMB- 1,2,4 TCB adduct. The distortion of the channel walls from the hexangonal arangement as in the R3bar space group, can be seen. The plane of the benzene ring can be

seen in the channel. Although the 1,2,4 TMB- 1,2,4 TCB molecules can not be modeled it is evident that the electron density is in a plane in the channel. This is consistent with the aromatic adducts studied by Welling (3) and Wick and Fitzgerald (15).

Even with the disorder in the channel, the thiourea molecules are fairly well defined. The thiourea network can be seen in Figures 13 and 14. This network is the same as the thiourea network in the other aromatic structures (3, 18). Hydrogen bonding between the sulfur atoms and adjacent NH_2 groups is evident. Four different lengths of hydrogen bonds were found. These lengths are 3.378A, 3.393A, 3.433A, and 3.452A. Even though the R value is fairly high, these lengths should be close enough to the actual values to give an idea of the nature of the hydrogen bonding. The hydrogen bond lengths in crystalline thiourea at room temperature are 3.394A, 3.526A, and 3.696A. As with the cis para-menthane adduct, the thiourea molecules are more tightly packed in the adduct than in crystalline thiourea. This tighter packing contributes to the lower energy of the adduct crystal structure in comparison to crystalline thiourea.

The spatial relationship between the thiourea
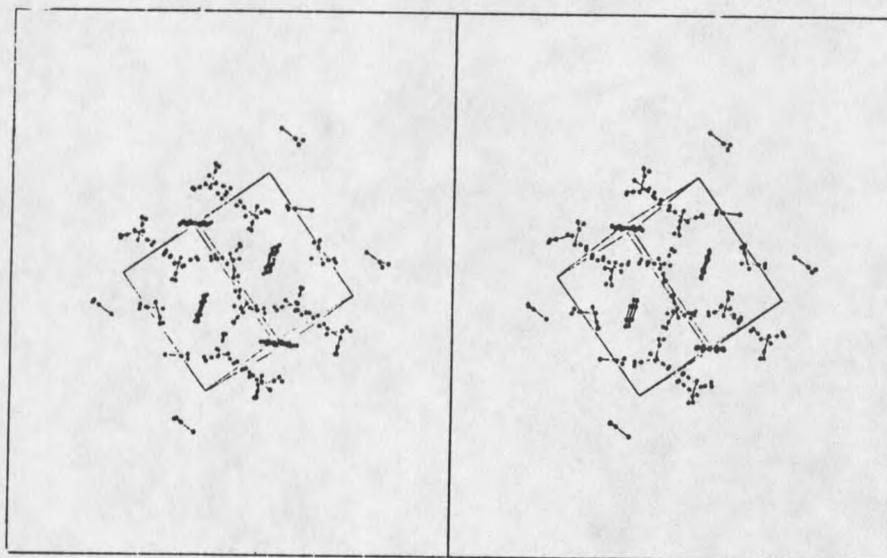
Figure 13

Stereoview of 1,2,4 TMB- 1,2,4 TCB thiourea adduct
viewed down the c-axis
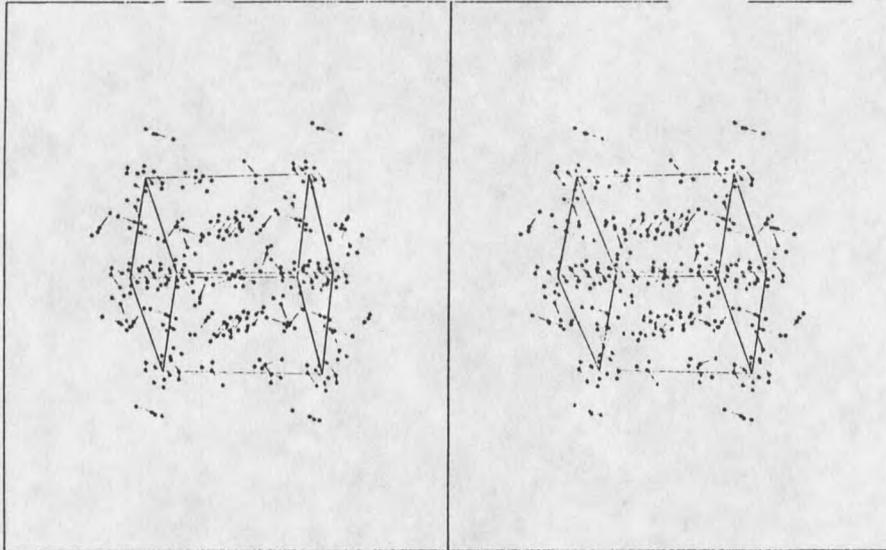
Figure 14

Stereoview of the 1,2,4 TMB- 1,2,4 TCB thiourea adduct
viewed down the c-axis offset by 20°

molecules and the plane of the aromatic rings is shown in Figures 15 and 16. Here the three planar sulfur atoms are pointing into the channel, but they are not in an equilateral triangle as in the cis para-menthane adduct. Figure 16 shows the two aromatic ring locations and the sulfur atoms pointing in at ring. It is evident that the molecules are orientated such as to allow the same type of interaction that was detected in the cis para-menthane adduct.
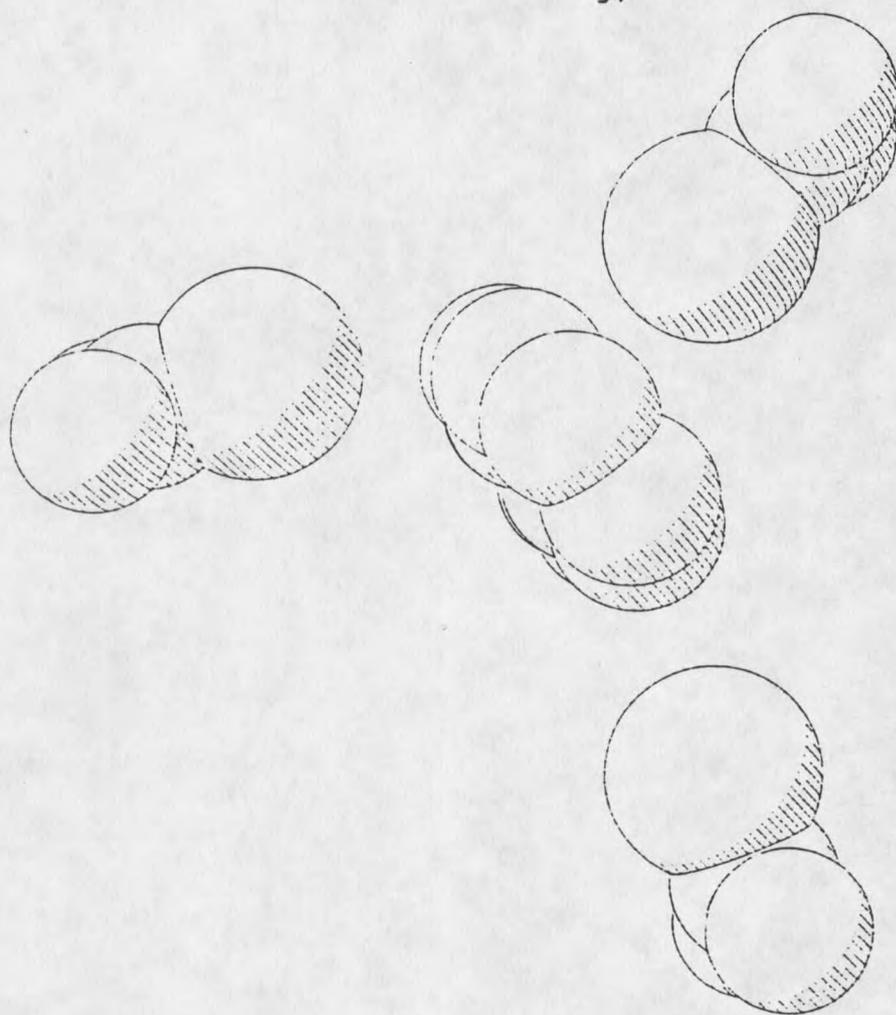
Figure 15

Three thiourea molecule with planar sulfur atoms and two
benzene rings from the 1,2,4 TMB- 1,2,4 TCB adduct
structure viewed down the c-axis
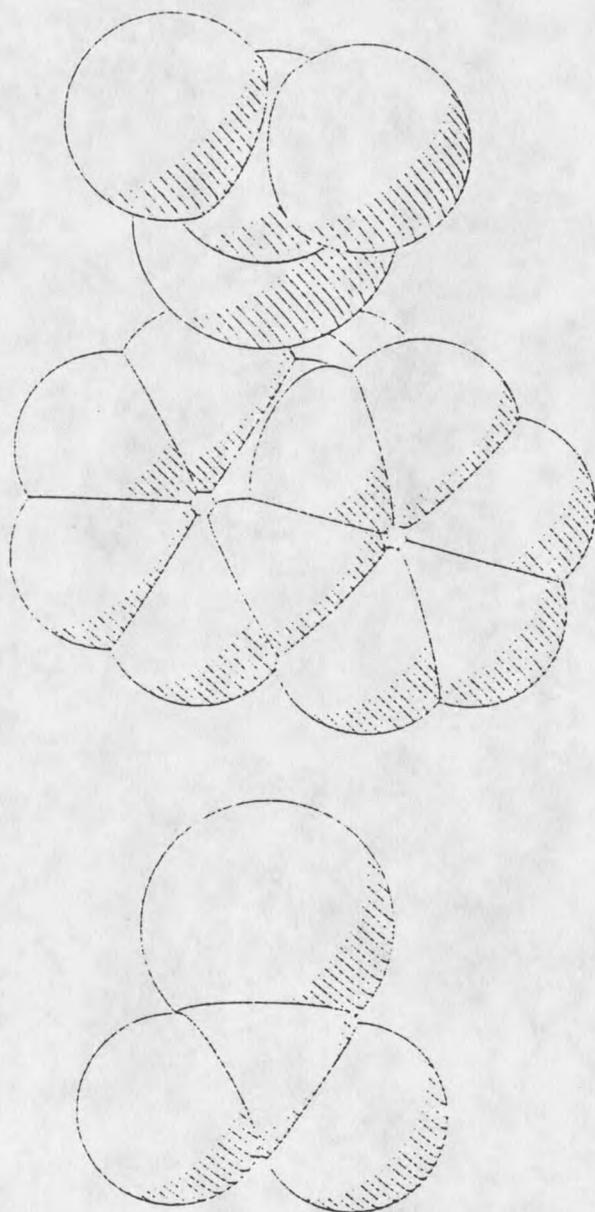
Figure 16

Two thiourea molecules with planar sulfur atoms and two
benzene rings from the 1,2,4 TMB- 1,2,4 TCB
adduct structure

Summary

Thiourea has the unusual ability to form adducts with a large number of hydrocarbons. In these adduct crystals the thiourea forms a cage-like network which traps the hydrocarbon molecule in a channel. Thiourea will selectively form adducts with some hydrocarbons over other hydrocarbons. This selective property is the basis for the process of extractive crystallization. Classes of hydrocarbons and isomers of a given empirical formula can be separated by extractive crystallization.

If the forces which hold thiourea adducts together were understood, then the selectivity might be understood. X-ray crystallographic studies have determined that the thiourea network is held together by hydrogen bonding, but this does not explain the selectivity of thiourea.

Structural data for thiourea adducts studied in work for this thesis and in related work is presented in Table 12. As can be seen the 1,2,4 TMB-1,2,4 TCB adduct is in the same space group and has a unit cell nearly the same size as the other aromatic adduct structures. The cis para-menthane adduct structure is quite similar to other non-aromatic adducts. One problem that has been encountered is the disorder of the hydrocarbon molecule in the channel. A

Table 12

Structural data of several thiourea adducts (all distances in A, numbers in parentheses are standard deviations)

Hydrocarbon Adducted with	A	B	C	α	β	γ	Space Group	DENSITY (g/cm^3)
Cyclohexane (14)	15.708(1)	15.708(1)	12.431(2)	90.0	90.0	120.0	R3bar	1.138
CCl_4 (14)	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 (3) 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 (3) 1,2,3 TMB							$P2_1/c$	1.3
1,2,4 TCB (15)	9.779(1)	15.355(1)	12.293(2)	90.0	111.85	90.0	$P2_1/c$	
1,2,4 TMB (3)	12.3 (1)	15.1 (1)	10.0 (2)	90.0	112.7	90.0	$P2_1/c$	1.11
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

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model that takes into account this disorder was found for the cis para-menthane molecule. Refinement of this model for the cis para-menthane adduct gave a R value of 0.067.

Schlenk was the first to recognize that every unit cell of the thiourea adducts contains a site of maximum attraction (10). These sites of maximum attraction occur because of three coplanar sulfur atoms pointing into the channel formed by the the thiourea molecules. Evidence, in the form of interatomic distances, for an interaction between these coplanar sulfur atoms and the C-H groups of the hydrocarbon molecule in the channel was found in the cis para-menthane adduct structure. This interaction is not a hydrogen bonding interaction, but probably an induced dipole-dipole interaction.

Conclusions

Thiourea's usual ability to form adducts with hydrocarbons shows promise as a method of separating hydrocarbon mixtures. It is not fully understood what forces hold these adducts together.

There are several strong indications of an interaction between the sulfur atoms and the hydrocarbon in the channel. As has been pointed out, thiourea will form adducts with some compounds while other compounds with the same number of carbons and a little different geometry due to the presence of an aromatic ring will not form adducts (see Table 1) and adducts with different included hydrocarbons vary widely in stability are both indications of an interaction. The strongest indication is that in the cis para-menthane adduct structure the sulfur atoms of thiourea molecules are almost at a distance equal to the sum of van der Waal radii distances from the hydrocarbon molecule. This proximity of the sulfur atoms to the carbon atoms of the enclosed hydrocarbon is an indication of a dipole-dipole attraction. Fetterly's postulation of a "supported hydrogen bond" is not consistent with this interaction. It is evident that the hydrocarbon in the channel is not "an otherwise inert surface capable of exerting only weak dispersion forces" as Fetterly claims (1).

The hydrocarbon molecule is involved in some form of interaction with the sulfur atom of the thiourea molecule. Hydrogen bonds are not possible between compounds such as carbon tetrachloride and the thiourea sulfur atoms, but an induced dipole-dipole attraction is possible. This interaction, along with the hydrogen bonds in the thiourea network, which are a lower energy bond than those in pure crystalline thiourea, combine to cause the adduct crystals to be in a lower energy state than the pure crystalline thiourea.

The geometry of the cis para-menthane is probably responsible for its selectivity over the trans isomer of para-menthane. The methyl group of the cis para-menthane molecule lies in the center of the channel, were as the methyl group of the trans isomer would lie closer to the sides of the channel. In this position the trans methyl group would be sterically hindered by the NH_2 group of a thiourea molecule. This steric hindrance could cause the trans para-menthane molecule to be distorted and therefore not to crystallize in a thiourea adduct as readily as the cis isomer.

A diffractometer data set was collected on a crystal containing a 50 mole percent mixture of 1,2,4 TMB and 1,2,4 TCB. The thiourea molecule positions were well defined, but

the hydrocarbon molecules were disordered. Attempts to model this disorder found no model which reduced the R value below 14%. Even with such a high R value, it is clear that the 1,2,4 TMB-1,2,4 TCB adduct structure is consistent with the structures studied by Welling (3) and Wick and Fitzgerald (15).

Recommendations

Thiourea forms adducts with a wide range of hydrocarbons. This large number of adducts with varying characteristics leads to many questions. One of these questions is the exact nature of the interaction between the thiourea molecules and the hydrocarbon in the channel. A study of the carbon tetrabromide adduct structure and other similar adducts may further define the interaction between the thiourea sulfur atom and the hydrocarbon molecule. The bromide atoms of carbon tetrabromide might be large enough to reduce the disorder problem. Welling's suggestion of a possible interaction between the chlorine atoms of TCB and the thiourea NH_2 groups of thiourea deserves further study. A less disordered TCB adduct structure would be necessary to locate the chlorine atoms.

The role of inductors was not been clarified by any of the adduct structures studied. It may be difficult to solve any adduct structure which contains more than one hydrocarbon in the channel. An adduct which would be of interest would be one which contained carbon tetrachloride and an aromatic molecule. The carbon tetrachloride-thiourea adduct crystallizes in the space group R3bar. The aromatic-thiourea adducts crystallize in the space group $P2_1/c$. It would be interesting to see in what space group an adduct

containing a mixture of carbon tetrachloride and an aromatic molecule, probably ethyl benzene (6), would crystalize.

The 1,2,4 TMB-1,2,4 TCB adduct structure may refine to a lower R value on a program package with full matrix least squares. The XTAL system of crystallographic programs would be the obvious choice.

On the next diffractometer data set collected on a thiourea adduct the possibilities of a super lattice should be studied closer.

The adduct containing trans para-menthane should be studied. This structure could be compared to the cis isomer structure to determine if the explaination for thioureas selectivity for the cis isomer is correct.

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APPENDICES

APPENDIX A

Additional Figures
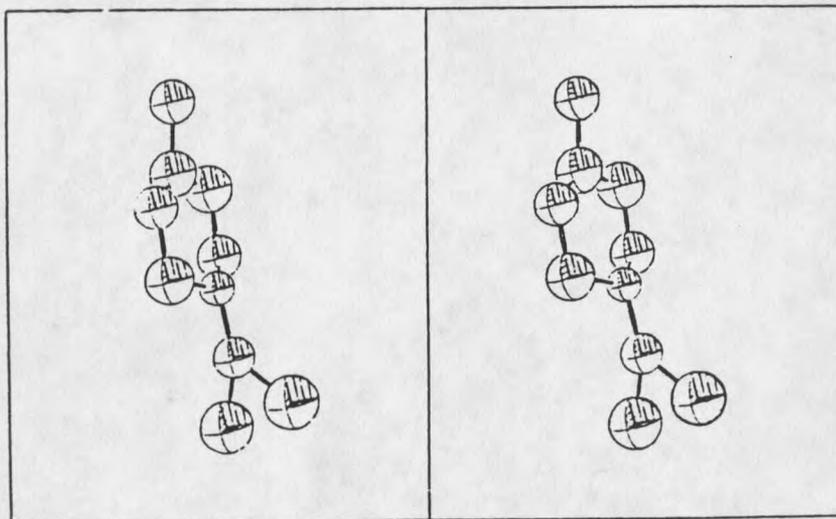
Figure 17

Stereoview of model for cis para-menthane molecule
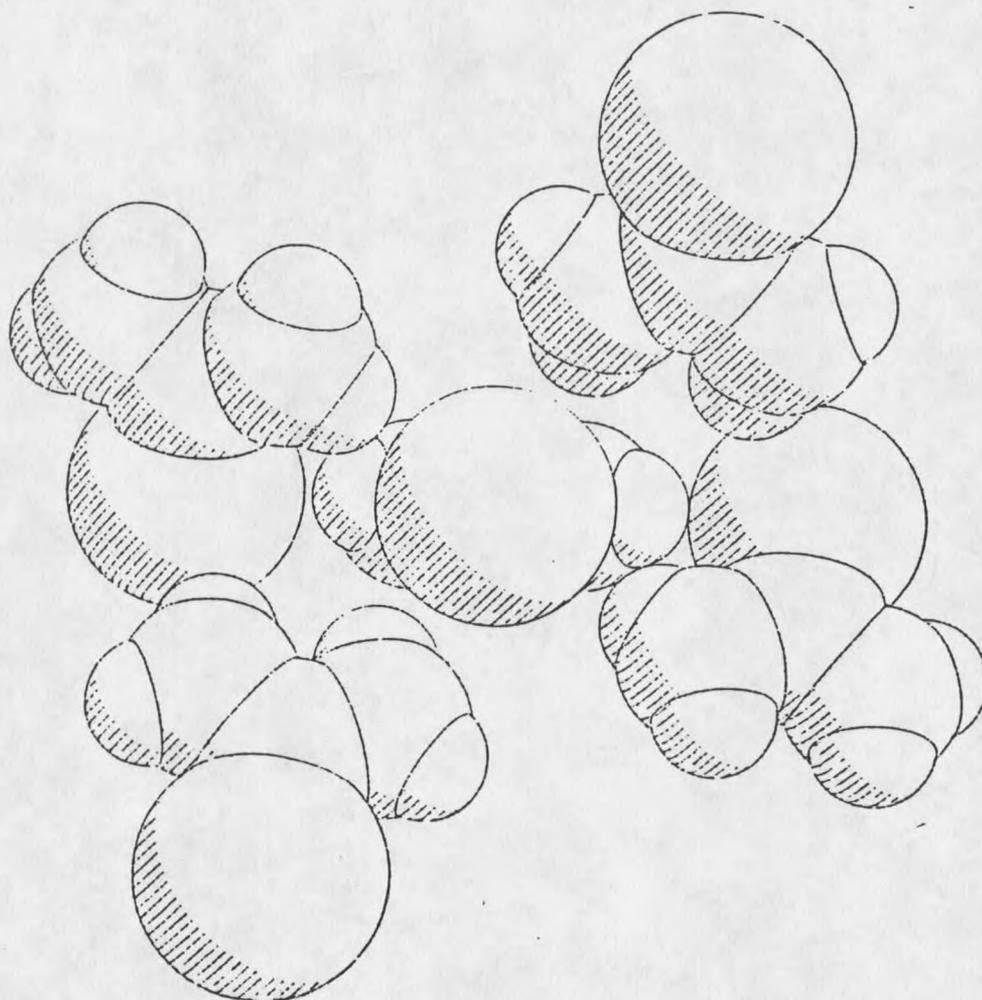
Figure 18

Thiourea molecules in the channel wall viewed in
at a sulfur pointing into the channel

APPENDIX B

Tables for Publication for
cis para-menthane adduct structure

Table 13

Atomic coordinates and isotropic thermal parameters for cis para-menthane adduct structure

Atomic coordinates $(\times 10^4)$ and isotropic thermal parameters $(\text{Å}^2 \times 10^3)$

	x	y	z	U
S(1)	−1(1)	2998(1)	2499(1)	61(1)*
C(1)	0(3)	4071(3)	2500(3)	59(1)*
N(1)	120(3)	4553(3)	1616(3)	83(1)*
N(2)	−121(3)	4426(3)	3396(3)	81(1)*
Cr(1)	−1026(4)	−297(15)	2989(7)	73(3)
Cr(2)	−1001(6)	−220(18)	1759(7)	123(3)
Cr(6)	17(3)	219(11)	3427(8)	118(3)
Cp(1)	−284(23)	735(17)	−298(7)	172(3)
Cm	0	0	4631(7)	78(3)
Cip	0	0	114(7)	84(3)
Cr(5)	1051(2)	615(16)	2989(7)	143(3)
Cr(4)	1036(4)	674(17)	1759(7)	107(3)
Cp(2)	160(25)	−821(16)	−298(7)	183(3)
Cr(3)	0	0	1347(7)	37(3)

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

Table 14

Anisotropic thermal parameters for cis para-menthane adduct structure

Anisotropic thermal parameters ($\mathring{A}^2 \times 10^3$)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	75(1)	62(1)	51(1)	3(1)	6(1)	38(1)
C(1)	61(2)	63(2)	56(2)	−0(1)	−1(1)	34(1)
N(1)	120(2)	69(2)	68(2)	5(2)	3(2)	52(2)
N(2)	116(2)	75(2)	67(2)	−6(1)	3(2)	58(2)

The anisotropic temperature factor exponent takes the form:

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

Table 15

H-atom coordinates and isotropic thermal parameters for cis para-menthane adduct structure

H—Atom coordinates ($\times 10^4$) and isotropic thermal parameters ($\mathring{A}^2 \times 10^3$)

	x	y	z	U
H(11)	207(22)	5111(22)	1719(23)	101(3)
H(21)	−112(21)	4906(22)	3389(23)	86(3)
H(22)	−107(22)	4158(23)	3978(25)	119(3)
H(12)	152(21)	4395(21)	1202(22)	62(3)

Table 16

Bond lengths for cis para-menthane adduct structure

Bond lengths (Å)

S(1)-C(1)	1.708(5)	C(1)-N(1)	1.303(6)
C(1)-N(2)	1.311(6)	N(1)-H(11)	0.837(38)
N(1)-H(12)	0.588(31)	N(2)-H(21)	0.757(39)
N(2)-H(22)	0.850(34)	Cr(1)-Cr(2)	1.540(13)
Cr(1)-Cr(6)	1.540(8)	Cr(1)-Cr(6a)	1.335(20)
Cr(1)-Cr(6b)	1.858(10)	Cr(1)-Cr(5a)	1.014(21)
Cr(1)-Cr(5b)	1.859(23)	Cr(1)-Cr(4a)	1.785(16)
Cr(2)-Cr(3)	1.540(12)	Cr(2)-Cp(1e)	1.827(13)
Cr(2)-Cr(5a)	1.785(17)	Cr(2)-Cr(4a)	0.804(24)
Cr(6)-Cm	1.540(14)	Cr(6)-Cr(5)	1.540(8)
Cr(6)-Cr(1a)	1.859(24)	Cr(6)-Cr(1b)	1.335(13)
Cr(6)-Cr(6a)	0.582(17)	Cr(6)-Cr(6b)	0.582(17)
Cr(6)-Cr(5a)	1.335(26)	Cr(6)-Cr(5b)	1.858(17)
Cp(1)-Cip	1.540(35)	Cp(1)-Cr(2b)	1.827(13)
Cp(1)-Cp(1c)	1.631(38)	Cp(1)-Cp(1e)	1.631(30)
Cp(1)-Cipa	1.469(37)	Cp(1)-Cp(2a)	0.764(17)
Cp(1)-Cp(2b)	1.601(46)	Cp(1)-Cp(2d)	1.297(44)
Cp(1)-Cr(3a)	1.956(29)	Cm-Cr(6a)	1.540(13)
Cm-Cr(6b)	1.540(13)	Cm-Cma	0.923(19)
Cip-Cp(2)	1.540(33)	Cip-Cr(3)	1.540(13)
Cip-Cp(1a)	1.469(37)	Cip-Cp(1b)	1.540(26)
Cip-Cp(1c)	1.469(27)	Cip-Cp(1d)	1.540(25)
Cip-Cp(1e)	1.470(26)	Cip-Cipa	0.285(18)
Cip-Cp(2a)	1.470(35)	Cip-Cp(2b)	1.540(25)
Cip-Cp(2c)	1.470(26)	Cip-Cp(2d)	1.540(24)
Cip-Cp(2e)	1.470(24)	Cip-Cr(3a)	1.825(13)
Cr(5)-Cr(4)	1.540(13)	Cr(5)-Cr(1a)	1.859(22)
Cr(5)-Cr(1b)	1.014(23)	Cr(5)-Cr(2c)	1.786(17)
Cr(5)-Cr(6a)	1.858(15)	Cr(5)-Cr(6b)	1.335(10)
Cr(4)-Cr(3)	1.540(8)	Cr(4)-Cr(1b)	1.785(17)
Cr(4)-Cr(2c)	0.805(25)	Cr(4)-Cp(2e)	1.985(19)
Cp(2)-Cp(1a)	0.764(17)	Cp(2)-Cp(1b)	1.297(49)
Cp(2)-Cp(1d)	1.601(42)	Cp(2)-Cipa	1.470(35)
Cp(2)-Cr(4b)	1.984(17)	Cp(2)-Cp(2c)	1.631(39)
Cp(2)-Cp(2e)	1.631(27)	Cp(2)-Cr(3a)	1.956(28)
Cr(3)-Cr(2a)	1.540(20)	Cr(3)-Cr(2c)	1.540(9)
Cr(3)-Cp(1a)	1.956(29)	Cr(3)-Cp(1c)	1.956(22)
Cr(3)-Cp(1e)	1.956(22)	Cr(3)-Cipa	1.825(13)
Cr(3)-Cr(4a)	1.540(25)	Cr(3)-Cr(4c)	1.540(7)
Cr(3)-Cp(2a)	1.956(28)	Cr(3)-Cp(2c)	1.956(21)
Cr(3)-Cp(2e)	1.956(20)		

Table 17

Bond angles for cis para-menthane adduct structure

Bond angles (°)

S(1)-C(1)-N(1)	121.1(4)	S(1)-C(1)-N(2)	120.3(3)
N(1)-C(1)-N(2)	118.6(5)	C(1)-N(1)-H(11)	113.1(21)
C(1)-N(1)-H(12)	120.6(33)	H(11)-N(1)-H(12)	125.9(37)
C(1)-N(2)-H(21)	119.6(22)	C(1)-N(2)-H(22)	117.7(27)
H(21)-N(2)-H(22)	121.8(34)	Cr(2)-Cr(1)-Cr(6)	109.5(6)
Cr(2)-Cr(1)-Cr(6a)	114.5(9)	Cr(6)-Cr(1)-Cr(6a)	21.9(7)
Cr(2)-Cr(1)-Cr(6b)	107.0(7)	Cr(6)-Cr(1)-Cr(6b)	16.6(7)
Cr(2)-Cr(1)-Cr(5a)	86.1(14)	Cr(6)-Cr(1)-Cr(5a)	58.8(15)
Cr(2)-Cr(1)-Cr(5b)	92.9(13)	Cr(6)-Cr(1)-Cr(5b)	65.5(9)
Cr(2)-Cr(1)-Cr(4a)	26.7(9)	Cr(6)-Cr(1)-Cr(4a)	93.1(10)
Cr(1)-Cr(2)-Cr(3)	109.5(9)	Cr(1)-Cr(2)-Cp(1e)	173.1(22)
Cr(3)-Cr(2)-Cp(1e)	70.4(9)	Cr(1)-Cr(2)-Cr(5a)	34.5(8)
Cr(3)-Cr(2)-Cr(5a)	98.0(9)	Cr(1)-Cr(2)-Cr(4a)	93.9(15)
Cr(3)-Cr(2)-Cr(4a)	74.9(19)	Cr(1)-Cr(6)-Cm	109.5(6)
Cr(1)-Cr(6)-Cr(5)	137.7(9)	Cm-Cr(6)-Cr(5)	109.5(7)
Cr(1)-Cr(6)-Cr(1a)	95.4(8)	Cm-Cr(6)-Cr(1a)	95.0(9)
Cr(5)-Cr(6)-Cr(1a)	65.6(12)	Cr(1)-Cr(6)-Cr(1b)	122.6(12)
Cm-Cr(6)-Cr(1b)	121.9(7)	Cr(5)-Cr(6)-Cr(1b)	40.5(9)
Cr(1)-Cr(6)-Cr(6a)	58.8(18)	Cm-Cr(6)-Cr(6a)	79.1(5)
Cr(5)-Cr(6)-Cr(6a)	114.5(12)	Cr(1)-Cr(6)-Cr(6b)	114.5(18)
Cm-Cr(6)-Cr(6b)	79.1(7)	Cr(5)-Cr(6)-Cr(6b)	58.8(12)
Cr(1)-Cr(6)-Cr(5a)	40.5(9)	Cm-Cr(6)-Cr(5a)	121.9(9)
Cr(5)-Cr(6)-Cr(5a)	122.6(10)	Cr(1)-Cr(6)-Cr(5b)	65.5(10)
Cm-Cr(6)-Cr(5b)	95.0(9)	Cr(5)-Cr(6)-Cr(5b)	95.5(12)
Cip-Cp(1)-Cr(2b)	109.4(19)	Cip-Cp(1)-Cp(1c)	55.1(8)
Cip-Cp(1)-Cp(1e)	55.1(8)	Cip-Cp(1)-Cipa	10.5(7)
Cip-Cp(1)-Cp(2a)	70.3(36)	Cip-Cp(1)-Cp(2b)	58.7(19)
Cip-Cp(1)-Cp(2d)	65.1(14)	Cip-Cp(1)-Cr(3a)	61.6(13)
Cr(6)-Cm-Cr(6a)	21.8(6)	Cr(6)-Cm-Cr(6b)	21.8(6)
Cr(6)-Cm-Cma	167.4(7)	Cp(1)-Cip-Cp(2)	140.4(11)
Cp(1)-Cip-Cr(3)	109.5(7)	Cp(2)-Cip-Cr(3)	109.5(6)
Cp(1)-Cip-Cp(1a)	169.5(7)	Cp(2)-Cip-Cp(1a)	29.3(8)
Cr(3)-Cip-Cp(1a)	81.0(6)	Cp(1)-Cip-Cp(1b)	109.4(7)
Cp(2)-Cip-Cp(1b)	49.8(18)	Cr(3)-Cip-Cp(1b)	109.5(6)
Cp(1)-Cip-Cp(1c)	65.6(6)	Cp(2)-Cip-Cp(1c)	127.7(18)
Cr(3)-Cip-Cp(1c)	81.0(5)	Cp(1)-Cip-Cp(1d)	109.4(6)
Cp(2)-Cip-Cp(1d)	62.6(15)	Cr(3)-Cip-Cp(1d)	109.5(6)
Cp(1)-Cip-Cp(1e)	65.6(4)	Cp(2)-Cip-Cp(1e)	114.6(15)
Cr(3)-Cip-Cp(1e)	81.0(5)	Cp(1)-Cip-Cipa	70.5(7)
Cp(2)-Cip-Cipa	70.5(6)	Cr(3)-Cip-Cipa	180.0(1)
Cp(1)-Cip-Cp(2a)	29.3(8)	Cp(2)-Cip-Cp(2a)	169.5(7)
Cr(3)-Cip-Cp(2a)	81.0(5)	Cp(1)-Cip-Cp(2b)	62.6(17)
Cp(2)-Cip-Cp(2b)	109.4(7)	Cr(3)-Cip-Cp(2b)	109.5(6)
Cp(1)-Cip-Cp(2c)	114.7(17)	Cp(2)-Cip-Cp(2c)	65.6(6)
Cr(3)-Cip-Cp(2c)	81.0(5)	Cp(1)-Cip-Cp(2d)	49.8(15)
Cp(2)-Cip-Cp(2d)	109.4(6)	Cr(3)-Cip-Cp(2d)	109.5(6)
Cp(1)-Cip-Cp(2e)	127.7(16)	Cp(2)-Cip-Cp(2e)	65.6(3)
Cr(3)-Cip-Cp(2e)	81.0(5)	Cp(1)-Cip-Cr(3a)	70.5(7)
Cp(2)-Cip-Cr(3a)	70.5(6)	Cr(3)-Cip-Cr(3a)	180.0(1)
Cr(6)-Cr(5)-Cr(4)	109.5(6)	Cr(6)-Cr(5)-Cr(1a)	65.5(11)

Table 17 (cont.)

Cr(4)-Cr(5)-Cr(1a)	92.9(12)	Cr(6)-Cr(5)-Cr(1b)	58.8(9)
Cr(4)-Cr(5)-Cr(1b)	86.1(15)	Cr(6)-Cr(5)-Cr(2c)	93.1(8)
Cr(4)-Cr(5)-Cr(2c)	26.7(10)	Cr(6)-Cr(5)-Cr(6a)	16.6(4)
Cr(4)-Cr(5)-Cr(6a)	107.0(5)	Cr(6)-Cr(5)-Cr(6b)	21.9(7)
Cr(4)-Cr(5)-Cr(6b)	114.5(7)	Cr(5)-Cr(4)-Cr(3)	109.5(6)
Cr(5)-Cr(4)-Cr(1b)	34.5(9)	Cr(3)-Cr(4)-Cr(1b)	98.0(6)
Cr(5)-Cr(4)-Cr(2c)	93.9(16)	Cr(3)-Cr(4)-Cr(2c)	74.8(8)
Cr(5)-Cr(4)-Cp(2e)	153.0(21)	Cr(3)-Cr(4)-Cp(2e)	66.0(11)
Cip-Cp(2)-Cp(1a)	70.2(35)	Cip-Cp(2)-Cp(1b)	65.1(23)
Cip-Cp(2)-Cp(1d)	58.7(9)	Cip-Cp(2)-Cipa	10.5(7)
Cip-Cp(2)-Cr(4b)	102.0(13)	Cip-Cp(2)-Cp(2c)	55.1(7)
Cip-Cp(2)-Cp(2e)	55.1(7)	Cip-Cp(2)-Cr(3a)	61.6(12)
Cr(2)-Cr(3)-Cip	109.5(5)	Cr(2)-Cr(3)-Cr(4)	132.4(10)
Cip-Cr(3)-Cr(4)	109.5(5)	Cr(2)-Cr(3)-Cr(2a)	109.4(5)
Cip-Cr(3)-Cr(2a)	109.5(5)	Cr(4)-Cr(3)-Cr(2a)	81.7(12)
Cr(2)-Cr(3)-Cr(2c)	109.4(9)	Cip-Cr(3)-Cr(2c)	109.5(5)
Cr(4)-Cr(3)-Cr(2c)	30.3(10)	Cr(2)-Cr(3)-Cp(1a)	127.7(11)
Cip-Cr(3)-Cp(1a)	47.9(8)	Cr(4)-Cr(3)-Cp(1a)	98.8(12)
Cr(2)-Cr(3)-Cp(1c)	122.3(14)	Cip-Cr(3)-Cp(1c)	47.9(6)
Cr(4)-Cr(3)-Cp(1c)	69.9(8)	Cr(2)-Cr(3)-Cp(1e)	61.7(6)
Cip-Cr(3)-Cp(1e)	47.9(6)	Cr(4)-Cr(3)-Cp(1e)	149.5(12)
Cr(2)-Cr(3)-Cipa	109.5(5)	Cip-Cr(3)-Cipa	0.0(1)
Cr(4)-Cr(3)-Cipa	109.5(5)	Cr(2)-Cr(3)-Cr(4a)	30.3(11)
Cip-Cr(3)-Cr(4a)	109.5(6)	Cr(4)-Cr(3)-Cr(4a)	109.4(6)
Cr(2)-Cr(3)-Cr(4c)	81.7(10)	Cip-Cr(3)-Cr(4c)	109.5(5)
Cr(4)-Cr(3)-Cr(4c)	109.4(10)	Cr(2)-Cr(3)-Cp(2a)	84.8(13)
Cip-Cr(3)-Cp(2a)	47.9(7)	Cr(4)-Cr(3)-Cp(2a)	102.1(12)
Cr(2)-Cr(3)-Cp(2c)	80.8(10)	Cip-Cr(3)-Cp(2c)	47.9(6)
Cr(4)-Cr(3)-Cp(2c)	146.8(11)	Cr(2)-Cr(3)-Cp(2e)	157.2(9)
Cip-Cr(3)-Cp(2e)	47.9(6)	Cr(4)-Cr(3)-Cp(2e)	68.0(10)

Table 18

F(obs) and sigma(F) for cis para-menthane adduct structure

h	k	l	10Fo	10s	h	k	l	10Fo	10s	h	k	l	10Fo	10s	h	k	l	10Fo	10s	h	k	l	10Fo	10s
-1	2	0	959	-5	-1	14	0	148	4	-8	6	1	1974	8	-1	10	1	119	5	-3	14	1	152	6
0	3	0	4790	28	-12	15	0	193	5	-5	6	1	2766	12	2	10	1	66	10	0	14	1	34	-23
-2	4	0	1694	5	-9	15	0	222	3	-2	6	1	245	2	5	10	1	99	8	3	14	1	64	15
-4	5	0	1668	7	-6	15	0	224	3	1	6	1	940	3	8	10	1	72	16	-17	15	1	95	10
-1	5	0	1669	6	-3	15	0	193	3	4	6	1	499	5	-18	11	1	57	16	-14	15	1	274	5
-3	6	0	316	2	0	15	0	103	7	-13	7	1	75	9	-15	11	1	311	4	-11	15	1	301	6
0	6	0	1072	4	-14	16	0	26	-21	-10	7	1	253	4	-12	11	1	736	3	-8	15	1	348	5
-5	7	0	430	2	-11	16	0	79	7	-7	7	1	37	13	-9	11	1	1102	8	-5	15	1	102	9
-2	7	0	431	2	-8	16	0	198	4	-4	7	1	234	5	-6	11	1	530	5	-2	15	1	169	8
-7	8	0	683	3	-5	16	0	91	7	-1	7	1	937	6	-3	11	1	153	5	1	15	1	170	6
-4	8	0	712	2	-2	16	0	38	-16	2	7	1	513	3	0	11	1	62	10	-16	16	1	48	-21
-1	8	0	682	2	-13	17	0	224	5	5	7	1	441	3	3	11	1	158	7	-13	16	1	47	-20
-6	9	0	318	2	-10	17	0	382	3	-15	8	1	338	4	6	11	1	47	-20	-10	16	1	25	-29
-3	9	0	323	2	-7	17	0	385	4	-12	8	1	532	3	-17	12	1	94	13	-7	16	1	25	-29
0	9	0	873	3	-4	17	0	220	5	-9	8	1	1515	10	-14	12	1	538	4	-4	16	1	141	6
-8	10	0	288	2	-12	18	0	159	6	-6	8	1	1998	16	-11	12	1	735	3	-1	16	1	166	10
-5	10	0	305	2	-9	18	0	166	6	-3	8	1	40	12	-8	12	1	536	7	-15	17	1	100	10
-2	10	0	287	2	-6	18	0	156	7	0	8	1	50	12	-5	12	1	443	3	-12	17	1	97	13
-10	11	0	106	5	-1	1	1	43	-2	3	8	1	156	5	-2	12	1	79	13	-9	17	1	84	12
-7	11	0	651	4	-3	2	1	403	4	6	8	1	361	4	1	12	1	311	4	-6	17	1	55	16
-4	11	0	650	3	0	2	1	63	2	-17	9	1	96	13	4	12	1	138	8	-3	17	1	81	11
-1	11	0	104	5	-5	3	1	2170	20	-14	9	1	464	3	-16	13	1	26	-30	-14	18	1	39	-24
-9	12	0	75	7	-2	3	1	403	3	-11	9	1	1095	4	-13	13	1	25	-29	-11	18	1	49	-21
-6	12	0	316	2	1	3	1	1990	4	-8	9	1	1520	12	-10	13	1	229	4	-8	18	1	63	16
-3	12	0	79	7	-7	4	1	237	2	-5	9	1	882	5	-7	13	1	73	9	-5	18	1	178	7
0	12	0	91	6	-4	4	1	68	12	-2	9	1	513	5	-4	13	1	152	6	0	1	2	320	4
-11	13	0	157	4	-1	4	1	1988	17	1	9	1	106	5	-1	13	1	308	4	-2	2	2	1332	13
-8	13	0	94	7	2	4	1	245	2	4	9	1	153	6	2	13	1	167	8	1	2	2	484	2
-5	13	0	87	7	-9	5	1	882	5	7	9	1	44	-20	5	13	1	181	7	-4	3	2	289	2
-2	13	0	168	3	-6	5	1	2750	14	-16	10	1	31	-24	-18	14	1	56	20	-1	3	2	484	4
-13	14	0	144	5	-3	5	1	2170	9	-13	10	1	224	4	-15	14	1	281	5	2	3	2	888	6
-10	14	0	384	2	0	5	1	51	10	-10	10	1	22	-25	-12	14	1	533	4	-6	4	2	110	4
-7	14	0	648	3	3	5	1	52	12	-7	10	1	256	4	-9	14	1	462	4	-3	4	2	290	2
-4	14	0	383	2	-11	6	1	521	2	-4	10	1	499	5	-6	14	1	357	3	0	4	2	1930	9

Table 18 (cont.)

F(obs) and sigma(F) (-sigma = unobserved):   CIS PARA-MENTHANE

h	k	l	10Fo	10s	h	k	l	10Fo	10s	h	k	l	10Fo	10s	h	k	l	10Fo	10s	h	k	l	10Fo	10s
3	4	2	1622	21	8	9	2	54	16	3	13	2	254	9	0	3	3	49	7	-9	9	3	57	15
-8	5	2	894	2	-18	10	2	73	14	-17	14	2	209	6	3	3	3	82	8	-6	9	3	269	4
-2	5	2	885	9	-15	10	2	52	18	-14	14	2	285	4	-5	4	3	1953	14	-3	9	3	235	3
1	5	2	1098	13	-12	10	2	87	9	-11	14	2	39	-21	-2	4	3	2434	3	0	9	3	27	-20
4	5	2	402	2	-9	10	2	52	12	-8	14	2	124	6	1	4	3	1341	2	3	9	3	252	4
-10	6	2	660	3	-6	10	2	663	3	-5	14	2	141	6	4	4	3	399	3	6	9	3	328	6
-7	6	2	64	8	-3	10	2	1375	15	-2	14	2	284	6	-7	5	3	1019	7	9	9	3	322	5
-4	6	2	116	4	0	10	2	1035	4	1	14	2	155	6	-4	5	3	1965	5	-17	10	3	27	-31
-1	6	2	1113	9	3	10	2	703	3	-16	15	2	177	6	-1	5	3	1365	4	-14	10	3	58	14
2	6	2	1215	6	6	10	2	188	5	-13	15	2	58	16	2	5	3	569	2	-11	10	3	71	13
5	6	2	463	3	-17	11	2	79	11	-10	15	2	40	-19	5	5	3	44	12	-8	10	3	80	16
-12	7	2	217	4	-14	11	2	72	12	-7	15	2	234	7	-9	6	3	272	3	-5	10	3	48	13
-9	7	2	172	5	-11	11	2	162	5	-4	15	2	212	7	-6	6	3	18	-21	-2	10	3	54	11
-6	7	2	54	8	-8	11	2	219	4	-1	15	2	164	6	-3	6	3	60	6	1	10	3	48	17
-3	7	2	1628	7	-5	11	2	465	3	2	15	2	73	16	0	6	3	31	-15	4	10	3	52	13
0	7	2	2320	12	-2	11	2	397	14	-15	16	2	166	7	3	6	3	245	3	7	10	3	75	17
3	7	2	1381	10	1	11	2	407	3	-12	16	2	73	18	6	6	3	193	5	-16	11	3	404	5
6	7	2	645	3	4	11	2	220	9	-9	16	2	102	9	-11	7	3	220	3	-13	11	3	148	5
-14	8	2	118	7	7	11	2	27	-38	-6	16	2	191	8	-8	7	3	161	5	-10	11	3	59	13
-11	8	2	217	3	-16	12	2	50	-20	-3	16	2	257	9	-5	7	3	1025	8	-7	11	3	220	5
-8	8	2	50	11	-13	12	2	97	8	0	16	2	136	8	-2	7	3	571	5	-4	11	3	152	4
-5	8	2	897	4	-10	12	2	96	9	-14	17	2	232	5	1	7	3	323	2	-1	11	3	23	-26
-2	8	2	1225	21	-7	12	2	219	4	-11	17	2	93	18	4	7	3	148	4	2	11	3	179	5
1	8	2	783	4	-4	12	2	628	5	-8	17	2	54	17	7	7	3	73	17	5	11	3	267	5
4	8	2	621	5	-1	12	2	410	4	-5	17	2	39	-23	-13	8	3	436	3	-18	12	3	268	6
7	8	2	225	4	2	12	2	276	4	-2	17	2	81	12	-10	8	3	71	11	-15	12	3	237	5
-16	9	2	105	15	5	12	2	78	11	-13	18	2	92	12	-7	8	3	171	6	-12	12	3	36	-21
-13	9	2	181	7	-18	13	2	102	10	-10	18	2	73	15	-4	8	3	397	4	-9	12	3	84	10
-10	9	2	61	12	-15	13	2	68	14	-7	18	2	47	-22	-1	8	3	327	6	-6	12	3	195	4
-7	9	2	175	4	-12	13	2	92	9	0	0	3	41	11	2	8	3	79	16	-3	12	3	260	6
-4	9	2	404	3	-9	13	2	187	4	1	1	3	3181	36	5	8	3	245	5	0	12	3	67	16
-1	9	2	785	6	-6	13	2	643	4	-1	2	3	3197	3	8	8	3	456	4	3	12	3	175	6
2	9	2	376	5	-3	13	2	704	3	2	2	3	2400	21	-15	9	3	438	4	6	12	3	214	7
5	9	2	150	8	0	13	2	575	3	-3	3	3	34	11	-12	9	3	74	10	-17	13	3	91	17

Table 18 (cont.)

F(obs) and sigma(F) (-sigma = unobserved):   CIS PARA-MENTHANE

h	k	l	10Fo	10s	h	k	l	10Fo	10s	h	k	l	10Fo	10s	h	k	l	10Fo	10s	h	k	l	10Fo	10s
-14	13	3	47	17	0	2	4	1867	22	-17	9	4	43	-20	4	12	4	76	12	1	2	5	1059	8
-11	13	3	141	6	-5	3	4	339	2	-14	9	4	239	4	-16	13	4	125	11	-4	3	5	1096	6
-8	13	3	436	3	-2	3	4	288	3	-11	9	4	782	3	-13	13	4	434	4	-1	3	5	1063	18
-5	13	3	244	4	1	3	4	928	6	-8	9	4	754	3	-10	13	4	716	5	2	3	5	407	4
-2	13	3	190	5	-7	4	4	965	5	-5	9	4	706	8	-7	13	4	382	6	-6	4	5	649	2
1	13	3	104	9	-4	4	4	478	4	-2	9	4	425	4	-4	13	4	61	12	-3	4	5	1092	5
4	13	3	45	-20	-1	4	4	928	9	1	9	4	278	5	-1	13	4	51	14	0	4	5	26	-16
-16	14	3	147	9	2	4	4	627	4	4	9	4	56	16	2	13	4	154	8	3	4	5	292	4
-13	14	3	60	15	-9	5	4	701	3	7	9	4	63	13	-15	14	4	147	7	-8	5	5	1127	5
-10	14	3	60	15	-6	5	4	519	3	-16	10	4	200	6	-12	14	4	106	7	-5	5	5	18	-21
-7	14	3	46	-19	-3	5	4	335	2	-13	10	4	714	4	-9	14	4	235	5	-2	5	5	406	3
-4	14	3	59	13	0	5	4	561	16	-10	10	4	1515	29	-6	14	4	106	10	1	5	5	411	2
-1	14	3	82	9	3	5	4	55	10	-7	10	4	1326	9	-3	14	4	129	6	4	5	5	975	4
2	14	3	128	8	-11	6	4	493	3	-4	10	4	707	7	0	14	4	192	6	-10	6	5	174	6
-15	15	3	35	-26	-8	6	4	458	3	-1	10	4	270	3	3	14	4	233	8	-7	6	5	393	5
-12	15	3	233	6	-5	6	4	521	4	2	10	4	87	12	-14	15	4	146	6	-4	6	5	645	5
-9	15	3	440	4	-2	6	4	627	7	5	10	4	84	9	-11	15	4	266	6	-1	6	5	413	3
-6	15	3	335	6	1	6	4	593	4	8	10	4	116	10	-8	15	4	116	12	2	6	5	1007	5
-3	15	3	191	6	4	6	4	705	5	-18	11	4	148	8	-5	15	4	88	9	5	6	5	692	3
0	15	3	26	-30	-13	7	4	377	4	-15	11	4	271	5	-2	15	4	141	6	-12	7	5	331	5
-14	16	3	133	7	-10	7	4	1327	7	-12	11	4	461	5	1	15	4	135	11	-9	7	5	316	3
-11	16	3	395	4	-7	7	4	1279	5	-9	11	4	786	5	-13	16	4	128	11	-6	7	5	394	4
-8	16	3	450	5	-4	7	4	967	8	-6	11	4	498	4	-10	16	4	191	5	-3	7	5	293	4
-5	16	3	269	8	-1	7	4	595	3	-3	11	4	148	6	-7	16	4	65	14	0	7	5	43	15
-2	16	3	152	8	2	7	4	428	3	0	11	4	132	10	-4	16	4	84	11	3	7	5	200	4
-13	17	3	64	16	5	7	4	121	13	3	11	4	98	13	-1	16	4	127	14	6	7	5	121	7
-10	17	3	43	-20	-15	8	4	99	9	6	11	4	114	8	-12	17	4	67	13	-14	8	5	24	-28
-7	17	3	55	17	-12	8	4	250	4	-17	12	4	67	13	-9	17	4	54	20	-11	8	5	177	9
-4	17	3	47	-21	-9	8	4	753	5	-14	12	4	96	9	-6	17	4	130	10	-8	8	5	43	14
-12	18	3	267	6	-6	8	4	460	3	-11	12	4	465	3	-3	17	4	233	10	-5	8	5	1121	6
-9	18	3	330	5	-3	8	4	61	8	-8	12	4	253	4	-11	18	4	143	8	-2	8	5	1000	6
-6	18	3	227	6	0	8	4	172	6	-5	12	4	105	8	-8	18	4	129	9	1	8	5	1271	4
-1	1	4	532	4	3	8	4	143	5	-2	12	4	75	11	0	1	5	22	-16	4	8	5	861	5
-3	2	4	286	3	6	8	4	88	10	1	12	4	57	14	-2	2	5	38	14	7	8	5	78	10

Table 18 (cont.)

F(obs) and sigma(F) (-sigma = unobserved):   CIS PARA-MENTHANE

h	k	l	10Fo	10s	h	k	l	10Fo	10s	h	k	l	10Fo	10s	h	k	l	10Fo	10s	h	k	l	10Fo	10s
-16	9	5	83	11	-12	13	5	44	-20	4	4	6	269	4	6	9	6	235	5	-4	14	6	316	8
-13	9	5	154	6	-9	13	5	143	8	-7	5	6	529	5	-17	10	6	379	7	-1	14	6	68	18
-10	9	5	185	4	-6	13	5	117	9	-4	5	6	448	3	-14	10	6	332	4	-15	15	6	120	10
-7	9	5	317	3	-3	13	5	101	9	-1	5	6	510	5	-11	10	6	118	6	-12	15	6	98	12
-4	9	5	974	11	0	13	5	56	18	2	5	6	517	3	-8	10	6	87	12	-9	15	6	227	8
-1	9	5	1265	10	3	13	5	83	11	5	5	6	162	4	-5	10	6	168	7	-6	15	6	223	6
2	9	5	890	4	-14	14	5	61	18	-9	6	6	59	12	-2	10	6	141	6	-3	15	6	49	-21
5	9	5	296	5	-11	14	5	93	9	-6	6	6	454	9	1	10	6	77	10	0	15	6	80	16
8	9	5	115	8	-8	14	5	44	-19	-3	6	6	1421	9	4	10	6	320	5	-11	16	6	159	7
-15	10	5	95	9	-5	14	5	305	8	0	6	6	602	6	7	10	6	389	5	-8	16	6	175	9
-12	10	5	169	8	-2	14	5	315	7	3	6	6	102	7	-16	11	6	148	7	-5	16	6	195	6
-9	10	5	189	4	1	14	5	123	13	6	6	6	48	15	-13	11	6	177	6	-10	17	6	375	4
-6	10	5	165	5	-13	15	5	199	5	-11	7	6	97	13	-10	11	6	125	7	-7	17	6	381	6
-3	10	5	201	5	-10	15	5	93	11	-8	7	6	92	8	-7	11	6	76	9	-1	1	7	23	-18
0	10	5	34	-23	-7	15	5	74	14	-5	7	6	530	2	-4	11	6	122	6	-3	2	7	500	3
3	10	5	98	8	-4	15	5	198	6	-2	7	6	519	4	-1	11	6	75	10	0	2	7	27	-18
6	10	5	132	7	-1	15	5	129	11	1	7	6	41	15	2	11	6	206	6	-5	3	7	370	2
-17	11	5	77	13	-12	16	5	154	9	4	7	6	117	6	5	11	6	183	6	-2	3	7	502	3
-14	11	5	90	9	-9	16	5	86	10	7	7	6	375	4	-15	12	6	111	8	1	3	7	431	4
-11	11	5	24	-28	-6	16	5	129	7	-13	8	6	166	5	-12	12	6	63	17	-7	4	7	120	5
-8	11	5	179	5	-3	16	5	105	9	-10	8	6	95	11	-9	12	6	33	-23	-4	4	7	34	-15
-5	11	5	694	5	-11	17	5	84	13	-7	8	6	82	7	-6	12	6	37	-21	-1	4	7	427	4
-2	11	5	889	5	-8	17	5	129	9	-4	8	6	263	4	-3	12	6	24	-28	2	4	7	376	3
1	11	5	717	4	-5	17	5	165	11	-1	8	6	22	-25	0	12	6	97	10	-9	5	7	801	4
4	11	5	196	6	0	0	6	1307	3	2	8	6	145	5	3	12	6	65	12	-6	5	7	548	3
-16	12	5	156	6	1	1	6	709	3	5	8	6	152	7	-14	13	6	107	10	-3	5	7	374	2
-13	12	5	39	-21	-1	2	6	708	3	8	8	6	170	10	-11	13	6	186	5	0	5	7	21	-24
-10	12	5	153	6	2	2	6	1719	20	-15	9	6	233	5	-8	13	6	157	5	3	5	7	757	8
-7	12	5	331	3	-3	3	6	2151	5	-12	9	6	59	13	-5	13	6	145	6	-11	6	7	592	6
-4	12	5	864	5	0	3	6	2218	3	-9	9	6	322	4	-2	13	6	201	6	-8	6	7	889	5
-1	12	5	710	5	3	3	6	1404	10	-6	9	6	113	27	1	13	6	69	13	-5	6	7	547	4
2	12	5	315	5	-5	4	6	449	2	-3	9	6	113	19	-13	14	6	103	16	-2	6	7	379	3
5	12	5	167	8	-2	4	6	1713	55	0	9	6	252	5	-10	14	6	324	4	1	6	7	286	3
-15	13	5	201	7	1	4	6	514	3	3	9	6	24	-28	-7	14	6	373	5	4	6	7	94	9

Table 18 (cont.)

F(obs) and sigma(F) (-sigma = unobserved):   CIS PARA-MENTHANE

h	k	l	10Fo	10s	h	k	l	10Fo	10s	h	k	l	10Fo	10s	h	k	l	10Fo	10s	h	k	l	10Fo	10s
-13	7	7	35	-21	-6	11	7	593	3	2	3	8	204	4	-4	9	8	307	4	-7	15	8	56	20
-10	7	7	128	14	-3	11	7	120	6	-6	4	8	274	3	-1	9	8	511	5	-4	15	8	171	8
-7	7	7	23	-27	0	11	7	40	-20	-3	4	8	312	4	2	9	8	424	4	0	0	9	26	-53
-4	7	7	128	5	3	11	7	66	15	0	4	8	595	5	5	9	8	153	6	1	1	9	1394	7
-1	7	7	286	3	-14	12	7	285	8	3	4	8	643	4	-15	10	8	50	18	-1	2	9	1384	11
2	7	7	179	4	-11	12	7	518	3	-8	5	8	244	4	-12	10	8	50	17	2	2	9	987	7
5	7	7	248	4	-8	12	7	629	4	-5	5	8	258	3	-9	10	8	157	5	-3	3	9	58	17
-15	8	7	63	14	-5	12	7	252	5	-2	5	8	199	4	-6	10	8	362	4	0	3	9	58	17
-12	8	7	631	3	-2	12	7	58	15	1	5	8	484	4	-3	10	8	772	9	3	3	9	206	6
-9	8	7	1003	5	1	12	7	50	17	4	5	8	303	5	0	10	8	921	4	-5	4	9	494	3
-6	8	7	897	5	4	12	7	138	8	-10	6	8	363	4	3	10	8	436	4	-2	4	9	986	5
-3	8	7	762	4	-13	13	7	26	-30	-7	6	8	278	3	-14	11	8	93	10	1	4	9	625	10
0	8	7	58	11	-10	13	7	26	-30	-4	6	8	279	5	-11	11	8	54	17	4	4	9	143	6
3	8	7	133	6	-7	13	7	43	-18	-1	6	8	478	4	-8	11	8	175	5	-7	5	9	328	5
6	8	7	80	10	-4	13	7	75	10	2	6	8	428	6	-5	11	8	334	4	-4	5	9	489	3
-14	9	7	332	5	-1	13	7	26	-30	5	6	8	338	6	-2	11	8	426	4	-1	5	9	627	8
-11	9	7	712	5	2	13	7	154	13	-12	7	8	63	17	1	11	8	309	4	2	5	9	455	6
-8	9	7	1005	8	-12	14	7	281	5	-9	7	8	59	12	4	11	8	169	7	5	5	9	33	-23
-5	9	7	805	5	-9	14	7	325	5	-6	7	8	279	6	-13	12	8	54	16	-9	6	9	90	13
-2	9	7	176	5	-6	14	7	74	13	-3	7	8	639	4	-10	12	8	40	-20	-6	6	9	54	13
1	9	7	90	8	-3	14	7	58	14	0	7	8	1017	6	-7	12	8	67	17	-3	6	9	204	4
4	9	7	73	10	0	14	7	48	-21	3	7	8	776	4	-4	12	8	173	5	0	6	9	42	-19
7	9	7	96	10	-11	15	7	175	7	6	7	8	254	5	-1	12	8	312	5	3	6	9	74	12
-16	10	7	134	7	-8	15	7	40	-23	-14	8	8	91	12	2	12	8	80	12	6	6	9	210	5
-13	10	7	26	-30	-5	15	7	71	15	-11	8	8	167	6	-12	13	8	63	13	-11	7	9	89	8
-10	10	7	37	-23	-2	15	7	161	7	-8	8	8	313	3	-9	13	8	83	14	-8	7	9	229	4
-7	10	7	114	7	-10	16	7	133	10	-5	8	8	248	5	-6	13	8	252	8	-5	7	9	325	4
-4	10	7	86	12	-7	16	7	101	9	-2	8	8	429	3	-3	13	8	427	5	-2	7	9	449	6
-1	10	7	90	8	-4	16	7	138	8	1	8	8	512	7	0	13	8	309	6	1	7	9	207	6
2	10	7	77	16	0	1	8	237	4	4	8	8	173	5	-11	14	8	87	12	4	7	9	64	13
5	10	7	57	17	-2	2	8	263	3	7	8	8	56	16	-8	14	8	83	11	7	7	9	68	19
-15	11	7	176	6	1	2	8	187	5	-13	9	8	96	9	-5	14	8	152	12	-13	8	9	203	5
-12	11	7	520	5	-4	3	8	317	4	-10	9	8	158	5	-2	14	8	67	14	-10	8	9	44	-20
-9	11	7	719	8	-1	3	8	188	3	-7	9	8	55	12	-10	15	8	83	11	-7	8	9	234	9

Table 18 (cont.)

F(obs) and sigma(F) (-sigma = unobserved):   CIS PARA-MENTHANE   Page 6

h	k	l	10Fo	10s	h	k	l	10Fo	10s	h	k	l	10Fo	10s	h	k	l	10Fo	10s	h	k	l	10Fo	10s
-4	8	9	150	5	-4	14	9	66	19	3	8	10	77	10	3	4	11	104	9	-8	11	11	53	17
-1	8	9	208	4	-1	1	10	92	11	-11	9	10	144	10	-8	5	11	61	13	-5	11	11	222	5
2	8	9	81	11	-3	2	10	194	8	-8	9	10	370	4	-5	5	11	36	-21	-2	11	11	366	6
5	8	9	251	5	0	2	10	316	4	-5	9	10	175	5	-2	5	11	408	3	-7	12	11	187	6
-12	9	9	147	6	-5	3	10	212	4	-2	9	10	90	17	1	5	11	681	5	-4	12	11	232	5
-9	9	9	25	-28	-2	3	10	201	4	1	9	10	67	16	4	5	11	372	4	0	0	12	1243	5
-6	9	9	91	17	1	3	10	34	-21	4	9	10	116	9	-10	6	11	158	9	1	1	12	518	7
-3	9	9	77	12	-7	4	10	583	4	-13	10	10	331	5	-7	6	11	237	4	-1	2	12	509	5
0	9	9	35	-21	-4	4	10	653	4	-10	10	10	477	7	-4	6	11	215	5	2	2	12	129	9
3	9	9	103	8	-1	4	10	23	-27	-7	10	10	533	6	-1	6	11	683	5	-3	3	12	689	5
-14	10	9	35	-25	2	4	10	71	13	-4	10	10	237	6	2	6	11	527	3	0	3	12	640	62
-11	10	9	68	17	-9	5	10	182	5	-1	10	10	43	-21	5	6	11	221	5	3	3	12	275	5
-8	10	9	59	16	-6	5	10	442	3	2	10	10	59	16	-12	7	11	187	6	-5	4	12	301	4
-5	10	9	36	-21	-3	5	10	202	4	-12	11	10	213	8	-9	7	11	178	7	-2	4	12	138	7
-2	10	9	68	14	0	5	10	48	14	-9	11	10	139	7	-6	7	11	246	4	1	4	12	273	4
1	10	9	68	13	3	5	10	285	4	-6	11	10	144	6	-3	7	11	123	11	4	4	12	105	10
4	10	9	27	-31	-11	6	10	129	9	-3	11	10	81	13	0	7	11	28	-33	-7	5	12	32	-26
-13	11	9	147	9	-8	6	10	409	4	0	11	10	109	9	3	7	11	33	-27	-4	5	12	305	4
-10	11	9	34	-22	-5	6	10	440	4	-11	12	10	212	6	-11	8	11	60	16	-1	5	12	274	7
-7	11	9	92	9	-2	6	10	86	13	-8	12	10	299	8	-8	8	11	42	-21	2	5	12	26	-30
-4	11	9	66	13	1	6	10	67	12	-5	12	10	125	8	-5	8	11	60	15	5	5	12	93	9
-1	11	9	64	14	4	6	10	232	6	-2	12	10	53	18	-2	8	11	534	5	-9	6	12	90	15
2	11	9	69	15	-13	7	10	285	8	-10	13	10	333	4	1	8	11	479	4	-6	6	12	302	7
-12	12	9	53	18	-10	7	10	529	7	-7	13	10	294	7	4	8	11	219	5	-3	6	12	276	4
-9	12	9	150	7	-7	7	10	903	3	-4	13	10	113	14	-10	9	11	27	-31	0	6	12	287	5
-6	12	9	212	5	-4	7	10	573	5	0	1	11	56	15	-7	9	11	176	6	3	6	12	118	13
-3	12	9	109	9	-1	7	10	72	13	-2	2	11	24	-28	-4	9	11	377	5	-11	7	12	107	10
0	12	9	46	-21	2	7	10	78	11	1	2	11	67	11	-1	9	11	476	4	-8	7	12	115	9
-11	13	9	158	10	5	7	10	142	7	-4	3	11	183	5	2	9	11	363	4	-5	7	12	64	14
-8	13	9	210	6	-12	8	10	305	4	-1	3	11	89	8	-9	10	11	67	17	-2	7	12	26	-30
-5	13	9	253	5	-9	8	10	368	4	2	3	11	400	5	-6	10	11	164	6	1	7	12	96	9
-2	13	9	85	19	-6	8	10	404	6	-6	4	11	213	5	-3	10	11	27	-31	4	7	12	133	12
-10	14	9	44	-19	-3	8	10	283	8	-3	4	11	184	5	0	10	11	50	-22	-10	8	12	27	-31
-7	14	9	27	-31	0	8	10	87	10	0	4	11	56	16	-11	11	11	46	-20	-7	8	12	107	8

Table 18 (cont.)

F(obs) and sigma(F) (-sigma = unobserved): CIS PARA-MENTHANE

h	k	l	10Fo	10s		h	k	l	10Fo	10s		h	k	l	10Fo	10s		h	k	l	10Fo	10s		h	k	l	10Fo	10s
-4	8	12	107	8		-7	11	12	108	9		-1	4	13	85	10		1	6	13	92	14		-4	3	14	88	11
-1	8	12	116	8		-4	11	12	123	8		2	4	13	121	14		-7	7	13	29	-33		-1	3	14	63	16
2	8	12	107	10		-1	1	13	50	17		-9	5	13	194	10		-4	7	13	51	18		2	3	14	136	10
-9	9	12	105	9		-3	2	13	87	10		-6	5	13	353	5		-1	7	13	82	11		-6	4	14	60	17
-6	9	12	88	10		0	2	13	44	-20		-3	5	13	265	5		-6	8	13	356	4		-3	4	14	106	8
-3	9	12	119	8		-5	3	13	265	4		0	5	13	35	-24		-3	8	13	112	11		0	4	14	223	8
0	9	12	182	6		-2	3	13	84	13		3	5	13	109	9		-5	9	13	195	6		-5	5	14	100	10
-8	10	12	82	18		1	3	13	86	11		-8	6	13	353	4		0	1	14	54	19		-2	5	14	140	8
-5	10	12	83	10		-7	4	13	44	-22		-5	6	13	355	7		-2	2	14	72	11		-4	6	14	37	-25
-2	10	12	109	12		-4	4	13	27	-31		-2	6	13	123	7		1	2	14	61	16						

Table 19

Observed and calculated structure factors for cis para-menthane adduct structure

Observed and calculated structure factors: CIS PARA-MENTHANE

h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc
0	3	0	3221	2481	-12	15	0	130	141	4	6	1	336	320	-9	11	1	741	736	-1	16	1	112	112
-2	4	0	1139	644	-9	15	0	149	168	-13	7	1	50	36	-6	11	1	356	364	-15	17	1	67	70
-4	5	0	1122	1088	-6	15	0	151	172	-10	7	1	170	166	-3	11	1	103	92	-12	17	1	65	64
-1	5	0	1122	1096	-3	15	0	130	135	-7	7	1	25	10	0	11	1	41	18	-9	17	1	57	52
-3	6	0	213	241	0	15	0	70	62	-4	7	1	157	167	3	11	1	106	107	-6	17	1	37	3
0	6	0	721	774	-11	16	0	53	58	-1	7	1	630	602	-17	12	1	63	73	-3	17	1	55	47
-5	7	0	289	342	-8	16	0	133	153	2	7	1	345	339	-14	12	1	361	364	-8	18	1	42	30
-2	7	0	290	365	-5	16	0	61	66	5	7	1	297	304	-11	12	1	494	510	-5	18	1	119	110
-7	8	0	460	421	-13	17	0	150	153	-15	8	1	227	225	-8	12	1	360	353	0	1	2	215	287
-4	8	0	479	375	-10	17	0	257	257	-12	8	1	358	348	-5	12	1	298	301	-2	2	2	896	922
-1	8	0	458	411	-7	17	0	259	263	-9	8	1	1018	960	-2	12	1	53	33	1	2	2	325	310
-6	9	0	214	222	-4	17	0	148	150	-6	8	1	1344	1301	1	12	1	209	204	-4	3	2	194	163
-3	9	0	217	234	-12	18	0	107	97	-3	8	1	27	16	4	12	1	93	92	-1	3	2	326	320
0	9	0	587	563	-9	18	0	112	94	0	8	1	34	4	-10	13	1	154	154	2	3	2	597	563
-8	10	0	193	225	-6	18	0	105	91	3	8	1	105	114	-7	13	1	49	50	-6	4	2	74	33
-5	10	0	205	199	-3	2	1	271	339	6	8	1	243	257	-4	13	1	103	95	-3	4	2	195	150
-2	10	0	193	214	0	2	1	43	52	-17	9	1	65	71	-1	13	1	207	209	0	4	2	1298	1242
-10	11	0	71	15	-5	3	1	1459	1282	-14	9	1	312	332	2	13	1	112	129	3	4	2	1091	1069
-7	11	0	438	394	-2	3	1	271	244	-11	9	1	737	751	5	13	1	122	119	-8	5	2	601	560
-4	11	0	437	429	1	3	1	1338	1341	-8	9	1	1022	980	-18	14	1	37	1	-2	5	2	595	527
-1	11	0	70	35	-7	4	1	159	143	-5	9	1	593	566	-15	14	1	189	192	1	5	2	738	709
-9	12	0	51	96	-4	4	1	46	12	-2	9	1	345	346	-12	14	1	359	353	4	5	2	270	288
-6	12	0	213	266	-1	4	1	1337	1322	1	9	1	72	58	-9	14	1	311	314	-10	6	2	444	443
-3	12	0	53	104	2	4	1	165	175	4	9	1	103	97	-6	14	1	240	254	-7	6	2	43	23
0	12	0	61	104	-9	5	1	593	560	-13	10	1	151	152	-3	14	1	102	105	-4	6	2	78	29
-11	13	0	105	76	-6	5	1	1849	1817	-7	10	1	172	177	3	14	1	43	44	-1	6	2	749	718
-8	13	0	63	99	-3	5	1	1459	1393	-4	10	1	335	325	-17	15	1	64	65	2	6	2	817	799
-5	13	0	59	89	0	5	1	34	49	-1	10	1	80	56	-14	15	1	184	191	5	6	2	311	303
-2	13	0	113	71	3	5	1	35	68	2	10	1	45	32	-11	15	1	203	206	-12	7	2	146	149
-13	14	0	97	75	-11	6	1	350	366	5	10	1	66	73	-8	15	1	234	221	-9	7	2	115	121
-10	14	0	258	197	-8	6	1	1327	1255	8	10	1	48	29	-5	15	1	69	83	-6	7	2	36	8
-7	14	0	435	398	-5	6	1	1860	1797	-18	11	1	38	7	-2	15	1	114	102	-3	7	2	1095	1087
-4	14	0	257	228	-2	6	1	164	139	-15	11	1	209	203	1	15	1	114	106	0	7	2	1560	1464
-1	14	0	100	77	1	6	1	632	562	-12	11	1	495	495	-4	16	1	95	72	3	7	2	928	913

Table 19 (cont.)

Observed and calculated structure factors: CIS PARA-MENTHANE

h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc
6	7	2	434	432	4	11	2	148	148	-14	17	2	156	149	-10	8	3	47	39	-3	12	3	175	185
-14	8	2	80	90	-13	12	2	66	80	-11	17	2	63	42	-7	8	3	115	102	0	12	3	45	11
-11	8	2	146	172	-10	12	2	65	34	-8	17	2	36	18	-4	8	3	267	269	3	12	3	118	120
-8	8	2	33	41	-7	12	2	147	151	-2	17	2	54	44	-1	8	3	220	206	6	12	3	144	144
-5	8	2	603	548	-4	12	2	422	423	-13	18	2	62	59	2	8	3	53	17	-17	13	3	61	37
-2	8	2	824	795	-1	12	2	275	290	-10	18	2	49	43	5	8	3	165	156	-14	13	3	32	27
1	8	2	526	537	2	12	2	186	190	0	0	3	28	63	8	8	3	307	300	-11	13	3	95	95
4	8	2	418	432	5	12	2	53	35	1	1	3	2139	2212	-15	9	3	295	306	-8	13	3	293	280
7	8	2	151	155	-18	13	2	69	56	-1	2	3	2149	2030	-12	9	3	50	62	-5	13	3	164	160
-16	9	2	71	64	-15	13	2	46	49	2	2	3	1614	1507	-9	9	3	39	9	-2	13	3	128	132
-13	9	2	122	117	-12	13	2	62	84	-3	3	3	23	43	-6	9	3	181	187	1	13	3	70	69
-10	9	2	41	48	-9	13	2	126	109	0	3	3	33	42	-3	9	3	158	162	-16	14	3	99	93
-7	9	2	118	116	-6	13	2	432	429	3	3	3	55	30	3	9	3	169	171	-13	14	3	40	29
-4	9	2	272	273	-3	13	2	474	480	-5	4	3	1313	1274	6	9	3	221	231	-10	14	3	40	22
-1	9	2	528	515	0	13	2	387	385	-2	4	3	1637	1531	9	9	3	217	227	-4	14	3	39	22
2	9	2	253	262	3	13	2	171	172	1	4	3	902	897	-14	10	3	39	21	-1	14	3	55	57
5	9	2	101	94	-17	14	2	140	141	4	4	3	269	284	-11	10	3	48	35	2	14	3	86	101
8	9	2	36	20	-14	14	2	192	180	-7	5	3	685	638	-8	10	3	54	17	-12	15	3	156	152
-18	10	2	49	39	-8	14	2	83	81	-4	5	3	1321	1263	-5	10	3	32	28	-9	15	3	296	292
-15	10	2	35	23	-5	14	2	95	98	-1	5	3	918	866	-2	10	3	36	10	-6	15	3	225	230
-12	10	2	59	41	-2	14	2	191	184	2	5	3	382	357	1	10	3	32	3	-3	15	3	129	123
-9	10	2	35	39	1	14	2	105	111	5	5	3	30	19	4	10	3	35	22	-14	16	3	90	88
-6	10	2	446	450	-16	15	2	119	111	-9	6	3	183	174	7	10	3	50	26	-11	16	3	265	270
-3	10	2	924	898	-13	15	2	39	52	-3	6	3	40	51	-16	11	3	272	267	-8	16	3	302	303
0	10	2	696	680	-7	15	2	157	158	3	6	3	165	152	-13	11	3	100	93	-5	16	3	181	180
3	10	2	473	464	-4	15	2	142	156	6	6	3	130	134	-10	11	3	40	37	-2	16	3	103	98
6	10	2	127	121	-1	15	2	110	108	-11	7	3	148	135	-7	11	3	148	137	-13	17	3	43	28
-17	11	2	53	34	2	15	2	49	35	-8	7	3	108	108	-4	11	3	102	107	-7	17	3	37	18
-14	11	2	49	16	-15	16	2	112	112	-5	7	3	689	636	2	11	3	120	114	-12	18	3	180	175
-11	11	2	109	71	-12	16	2	49	43	-2	7	3	384	342	5	11	3	179	177	-9	18	3	222	224
-8	11	2	147	167	-9	16	2	68	64	1	7	3	217	204	-18	12	3	181	179	-6	18	3	153	148
-5	11	2	313	298	-6	16	2	128	136	4	7	3	100	100	-15	12	3	160	166	-1	1	4	358	582
-2	11	2	267	266	-3	16	2	173	174	7	7	3	49	23	-9	12	3	56	45	-3	2	4	193	110
1	11	2	273	278	0	16	2	92	91	-13	8	3	293	279	-6	12	3	131	139	0	2	4	1256	1019

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Table 19 (cont.)

Observed and calculated structure factors: CIS PARA-MENTHANE

h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc
-5	3	4	228	236	-11	9	4	526	519	-13	13	4	292	298	2	3	5	273	261	2	9	5	598	603
-2	3	4	194	84	-8	9	4	507	527	-10	13	4	482	477	-6	4	5	437	469	5	9	5	199	217
1	3	4	624	650	-5	9	4	475	498	-7	13	4	257	256	-3	4	5	734	729	8	9	5	77	76
-7	4	4	649	596	-2	9	4	286	310	-4	13	4	41	50	3	4	5	196	190	-15	10	5	64	62
-4	4	4	321	379	1	9	4	187	176	-1	13	4	34	14	-8	5	5	757	740	-12	10	5	113	109
-1	4	4	624	618	4	9	4	38	44	2	13	4	103	92	-2	5	5	273	259	-9	10	5	127	119
2	4	4	421	466	7	9	4	42	34	-15	14	4	99	94	1	5	5	276	287	-6	10	5	111	111
-9	5	4	471	494	-16	10	4	134	137	-12	14	4	71	68	4	5	5	656	669	-3	10	5	135	143
-6	5	4	349	382	-13	10	4	480	475	-9	14	4	158	154	-10	6	5	117	113	3	10	5	66	60
-3	5	4	225	211	-10	10	4	1018	1018	-6	14	4	71	46	-7	6	5	264	256	6	10	5	89	90
0	5	4	377	431	-7	10	4	891	847	-3	14	4	86	81	-4	6	5	434	456	-17	11	5	52	35
3	5	4	37	21	-4	10	4	475	478	0	14	4	129	141	-1	6	5	278	286	-14	11	5	61	66
-11	6	4	332	332	-1	10	4	181	191	3	14	4	157	153	2	6	5	677	662	-8	11	5	120	124
-8	6	4	308	329	2	10	4	59	45	-14	15	4	98	95	5	6	5	465	467	-5	11	5	467	488
-5	6	4	350	396	5	10	4	56	59	-11	15	4	179	186	-12	7	5	222	225	-2	11	5	598	614
-2	6	4	421	442	8	10	4	78	75	-8	15	4	78	69	-9	7	5	213	224	1	11	5	482	478
1	6	4	399	356	-18	11	4	99	102	-5	15	4	59	46	-6	7	5	265	236	4	11	5	132	130
4	6	4	474	464	-15	11	4	182	184	-2	15	4	95	87	-3	7	5	197	180	-16	12	5	105	104
-13	7	4	253	263	-12	11	4	310	305	1	15	4	90	79	0	7	5	29	8	-10	12	5	103	101
-10	7	4	892	857	-9	11	4	528	524	-13	16	4	86	92	3	7	5	134	150	-7	12	5	223	215
-7	7	4	860	835	-6	11	4	335	337	-10	16	4	129	135	6	7	5	81	72	-4	12	5	581	562
-4	7	4	650	595	-3	11	4	100	101	-7	16	4	44	29	-11	8	5	119	123	-1	12	5	478	475
-1	7	4	400	360	0	11	4	89	94	-4	16	4	57	51	-8	8	5	29	4	2	12	5	212	227
2	7	4	288	315	3	11	4	66	82	-1	16	4	85	78	-5	8	5	754	746	5	12	5	113	116
5	7	4	81	81	6	11	4	77	81	-12	17	4	45	50	-2	8	5	673	665	-15	13	5	135	127
-15	8	4	66	79	-17	12	4	45	46	-9	17	4	36	9	1	8	5	854	850	-9	13	5	96	96
-12	8	4	168	164	-14	12	4	65	72	-6	17	4	87	74	4	8	5	579	564	-6	13	5	79	73
-9	8	4	506	521	-11	12	4	313	315	-3	17	4	157	150	7	8	5	53	38	-3	13	5	68	65
-6	8	4	309	319	-8	12	4	170	164	-11	18	4	96	98	-16	9	5	56	55	0	13	5	37	4
-3	8	4	41	8	-5	12	4	71	68	-8	18	4	87	65	-13	9	5	104	97	3	13	5	56	69
0	8	4	116	150	-2	12	4	50	35	-2	2	5	26	31	-10	9	5	125	121	-14	14	5	41	3
3	8	4	96	101	1	12	4	38	17	1	2	5	712	714	-7	9	5	213	206	-11	14	5	63	65
6	8	4	59	43	4	12	4	51	55	-4	3	5	737	686	-4	9	5	655	660	-5	14	5	205	224
-14	9	4	161	146	-16	13	4	84	92	-1	3	5	715	705	-1	9	5	850	847	-2	14	5	212	225

Table 19 (cont.)

Observed and calculated structure factors: CIS PARA-MENTHANE

h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc
1	14	5	82	81	6	6	6	32	24	-7	11	6	51	56	-7	4	7	81	84	-16	10	7	90	95
-13	15	5	134	126	-11	7	6	65	45	-4	11	6	82	78	-1	4	7	287	285	-7	10	7	77	78
-10	15	5	63	68	-8	7	6	62	57	-1	11	6	51	38	2	4	7	253	266	-4	10	7	58	54
-7	15	5	50	32	-5	7	6	356	350	2	11	6	139	135	-9	5	7	538	558	-1	10	7	60	62
-4	15	5	133	126	-2	7	6	349	359	5	11	6	123	125	-6	5	7	369	386	2	10	7	52	36
-1	15	5	87	80	1	7	6	28	5	-15	12	6	74	72	-3	5	7	252	244	5	10	7	38	35
-12	16	5	104	104	4	7	6	79	85	-12	12	6	43	6	3	5	7	509	485	-15	11	7	118	115
-9	16	5	58	61	7	7	6	252	244	0	12	6	65	52	-11	6	7	398	394	-12	11	7	349	352
-6	16	5	87	96	-13	8	6	112	116	3	12	6	44	34	-8	6	7	597	582	-9	11	7	484	489
-3	16	5	71	66	-10	8	6	64	50	-14	13	6	72	69	-5	6	7	368	393	-6	11	7	399	412
-11	17	5	57	39	-7	8	6	55	43	-11	13	6	125	115	-2	6	7	255	292	-3	11	7	81	96
-8	17	5	87	85	-4	8	6	177	158	-8	13	6	105	106	1	6	7	192	183	3	11	7	45	32
-5	17	5	111	122	2	8	6	97	94	-5	13	6	98	111	4	6	7	63	65	-14	12	7	192	190
0	0	6	879	701	5	8	6	102	94	-2	13	6	135	142	-10	7	7	86	67	-11	12	7	348	345
1	1	6	477	562	8	8	6	114	121	1	13	6	47	35	-4	7	7	86	93	-8	12	7	423	411
-1	2	6	476	570	-15	9	6	157	152	-13	14	6	69	68	-1	7	7	193	188	-5	12	7	170	164
2	2	6	1156	1137	-12	9	6	40	43	-10	14	6	218	223	2	7	7	120	126	-2	12	7	39	35
-3	3	6	1446	1345	-9	9	6	216	214	-7	14	6	251	250	5	7	7	167	176	1	12	7	34	19
0	3	6	1492	1392	-6	9	6	76	40	-4	14	6	213	219	-15	8	7	42	49	4	12	7	93	87
3	3	6	944	936	-3	9	6	76	49	-1	14	6	46	46	-12	8	7	425	430	-4	13	7	50	61
-5	4	6	302	281	0	9	6	170	181	-15	15	6	81	77	-9	8	7	674	686	2	13	7	104	103
-2	4	6	1152	1141	6	9	6	158	157	-12	15	6	66	67	-6	8	7	603	583	-12	14	7	189	194
1	4	6	346	326	-17	10	6	255	255	-9	15	6	153	155	-3	8	7	512	493	-9	14	7	219	222
4	4	6	181	146	-14	10	6	223	224	-6	15	6	150	153	0	8	7	39	1	-6	14	7	50	50
-7	5	6	356	344	-11	10	6	80	73	0	15	6	54	29	3	8	7	89	82	-3	14	7	39	32
-4	5	6	301	300	-8	10	6	58	62	-11	16	6	107	102	6	8	7	54	50	-11	15	7	118	102
-1	5	6	343	340	-5	10	6	113	95	-8	16	6	118	124	-14	9	7	223	220	-5	15	7	48	42
2	5	6	348	339	-2	10	6	95	78	-5	16	6	131	129	-11	9	7	479	479	-2	15	7	108	114
5	5	6	109	96	1	10	6	51	38	-10	17	6	252	253	-8	9	7	676	678	-10	16	7	89	89
-9	6	6	40	39	4	10	6	215	208	-7	17	6	256	260	-5	9	7	542	551	-7	16	7	68	65
-6	6	6	305	324	7	10	6	261	261	-3	2	7	336	372	-2	9	7	119	120	-4	16	7	93	86
-3	6	6	956	928	-16	11	6	100	109	-5	3	7	249	236	1	9	7	61	44	0	1	8	159	125
0	6	6	405	418	-13	11	6	119	123	-2	3	7	338	334	4	9	7	49	40	-2	2	8	177	210
3	6	6	68	72	-10	11	6	84	68	1	3	7	290	283	7	9	7	65	69	1	2	8	126	137

Table 19 (cont.)

h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc
-4	3	8	213	237	-10	9	8	106	108	-10	15	8	56	33	5	8	9	169	162	0	5	10	32	46
-1	3	8	126	143	-7	9	8	37	29	-7	15	8	37	41	-12	9	9	99	103	3	5	10	191	175
2	3	8	137	111	-4	9	8	206	206	-4	15	8	115	112	-6	9	9	61	42	-11	6	10	87	96
-6	4	8	184	166	-1	9	8	344	350	1	1	9	937	940	-3	9	9	52	60	-8	6	10	275	274
-3	4	8	210	224	2	9	8	285	287	-1	2	9	930	927	3	9	9	70	66	-5	6	10	296	281
0	4	-8	400	431	5	9	8	103	97	2	2	9	663	661	-11	10	9	46	7	-2	6	10	58	50
3	4	8	432	478	-15	10	8	33	29	-3	3	9	39	11	-8	10	9	40	9	1	6	10	45	49
-8	5	8	164	137	-12	10	8	34	24	0	3	9	39	7	-2	10	9	46	37	4	6	10	156	168
-5	5	8	173	149	-9	10	8	106	115	3	3	9	139	135	1	10	9	46	35	-13	7	10	192	189
-2	5	8	134	116	-6	10	8	244	254	-5	4	9	332	318	-13	11	9	99	95	-10	7	10	356	370
1	5	8	326	294	-3	10	8	519	525	-2	4	9	663	633	-7	11	9	62	57	-7	7	10	607	623
4	5	8	204	197	0	10	8	619	631	1	4	9	421	419	-4	11	9	44	15	-4	7	10	385	407
-10	6	8	244	254	3	10	8	293	304	4	4	9	96	91	-1	11	9	43	43	-1	7	10	48	52
-7	6	8	187	215	-14	11	8	63	53	-7	5	9	221	216	2	11	9	46	29	2	7	10	52	55
-4	6	8	188	179	-11	11	8	36	27	-4	5	9	329	340	-12	12	9	36	8	5	7	10	95	88
-1	6	8	321	310	-8	11	8	118	112	-1	5	9	422	445	-9	12	9	101	95	-12	8	10	205	208
2	6	8	288	266	-5	11	8	225	225	2	5	9	306	306	-6	12	9	143	138	-9	8	10	247	240
5	6	8	227	217	-2	11	8	286	285	-9	6	9	61	53	-3	12	9	73	69	-6	8	10	272	272
-12	7	8	42	14	1	11	8	208	210	-6	6	9	36	17	-11	13	9	107	91	-3	8	10	190	187
-9	7	8	40	24	4	11	8	113	114	-3	6	9	137	159	-8	13	9	141	133	0	8	10	59	53
-6	7	8	187	216	-13	12	8	36	15	3	6	9	50	52	-5	13	9	170	167	3	8	10	52	48
-3	7	8	429	456	-7	12	8	45	10	6	6	9	141	135	-2	13	9	57	38	-11	9	10	97	97
0	7	8	684	715	-4	12	8	117	118	-11	7	9	60	49	-4	14	9	44	10	-8	9	10	249	246
3	7	8	522	533	-1	12	8	209	203	-8	7	9	154	142	-1	1	10	62	48	-5	9	10	118	121
6	7	8	171	171	2	12	8	54	48	-5	7	9	219	181	-3	2	10	131	122	-2	9	10	60	50
-14	8	8	61	56	-12	13	8	42	18	-2	7	9	302	279	0	2	10	212	192	1	9	10	45	1
-11	8	8	112	117	-9	13	8	56	56	1	7	9	139	126	-5	3	10	143	127	4	9	10	78	72
-8	8	8	210	202	-6	13	8	170	170	4	7	9	43	23	-2	3	10	135	126	-13	10	10	222	217
-5	8	8	167	150	-3	13	8	287	294	7	7	9	46	25	-7	4	10	392	415	-10	10	10	321	327
-2	8	8	288	269	0	13	8	208	215	-13	8	9	137	139	-4	4	10	439	440	-7	10	10	358	372
1	8	8	344	338	-11	14	8	58	68	-7	8	9	158	153	2	4	10	48	40	-4	10	10	160	164
4	8	8	116	121	-8	14	8	56	49	-4	8	9	101	109	-9	5	10	122	119	2	10	10	40	27
7	8	8	37	33	-5	14	8	102	92	-1	8	9	140	140	-6	5	10	297	272	-12	11	10	143	145
-13	9	8	65	52	-2	14	8	45	46	2	8	9	54	45	-3	5	10	135	128	-9	11	10	93	87

Table 19 (cont.)

Observed and calculated structure factors: CIS PARA-MENTHANE

h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc	h	k	l	10Fo	10Fc
-6	11	10	97	97	-7	6	11	159	159	-4	12	11	156	153	1	7	12	65	77	-6	5	13	238	249
-3	11	10	54	50	-4	6	11	145	149	0	0	12	836	824	4	7	12	90	81	-3	5	13	178	180
0	11	10	73	66	-1	6	11	459	468	1	1	12	349	362	-7	8	12	72	74	3	5	13	73	74
-11	12	10	142	144	2	6	11	354	368	-1	2	12	342	356	-4	8	12	72	81	-8	6	13	237	245
-8	12	10	201	205	5	6	11	148	152	2	2	12	87	95	-1	8	12	78	75	-5	6	13	239	256
-5	12	10	84	90	-12	7	11	126	123	-3	3	12	464	456	2	8	12	72	67	-2	6	13	83	83
-2	12	10	35	26	-9	7	11	120	126	0	3	12	430	445	-9	9	12	70	70	1	6	13	62	52
-10	13	10	224	219	-6	7	11	165	153	3	3	12	185	176	-6	9	12	59	55	-4	7	13	34	10
-7	13	10	198	193	-3	7	11	83	67	-5	4	12	202	191	-3	9	12	80	69	-1	7	13	55	53
-4	13	10	76	68	-11	8	11	41	37	-2	4	12	93	94	0	9	12	122	107	-6	8	13	239	242
0	1	11	38	1	-5	8	11	40	35	1	4	12	183	186	-8	10	12	55	38	-3	8	13	75	73
1	2	11	45	50	-2	8	11	359	366	4	4	12	70	73	-5	10	12	56	60	-5	9	13	131	138
-4	3	11	123	121	1	8	11	322	332	-4	5	12	205	203	-2	10	12	73	79	0	1	14	36	21
-1	3	11	60	52	4	8	11	147	153	-1	5	12	184	195	-7	11	12	73	84	-2	2	14	49	29
2	3	11	269	276	-7	9	11	118	125	5	5	12	63	58	-4	11	12	82	85	1	2	14	41	29
-6	4	11	143	145	-4	9	11	253	247	-9	6	12	60	49	-1	1	13	34	6	-4	3	14	59	51
-3	4	11	124	128	-1	9	11	320	333	-6	6	12	203	196	-3	2	13	58	56	-1	3	14	42	34
0	4	11	37	2	2	9	11	244	254	-3	6	12	185	189	-5	3	13	179	175	2	3	14	91	97
3	4	11	70	72	-9	10	11	45	30	0	6	12	193	188	-2	3	13	57	63	-6	4	14	41	19
-8	5	11	41	44	-6	10	11	110	99	3	6	12	80	64	1	3	13	58	49	-3	4	14	71	56
-2	5	11	274	280	-8	11	11	35	37	-11	7	12	72	78	-1	4	13	57	57	0	4	14	150	155
1	5	11	458	466	-5	11	11	149	149	-8	7	12	77	75	2	4	13	81	82	-5	5	14	67	52
4	5	11	250	255	-2	11	11	246	255	-5	7	12	43	10	-9	5	13	130	140	-2	5	14	94	92
-10	6	11	106	108	-7	12	11	126	120																

APPENDIX C

Atomic Positions for 1,2,4 TMB-1,2,4 TCB Thiourea Adduct Structure

Table 20

Atomic positions from 1,2,4 TMB-1,2,4 TCB thiourea
adduct structure (B1-B6, T1-T6, R1-R6 and
C20-C25 are idealized benzene rings)

Atom	X	Y	Z
S1	-0.00556	0.63838	0.13959
C1	0.09079	0.70967	0.09028
N11	0.03603	0.74909	-0.01069
N12	0.23024	0.72774	0.15538
S2	0.39843	0.64885	0.43859
C2	0.27982	0.68994	0.49538
N21	0.32437	0.77146	0.60626
N22	0.13921	0.69558	0.43244
S3	0.31607	0.30130	0.20406
C3	0.27668	0.40610	0.22302
N31	0.33151	0.44722	0.32590
N32	0.18305	0.45126	0.13518
B1	0.25286	-0.06582	0.39206
B2	0.22353	-0.02192	0.28610
B3	0.32826	0.03401	0.27349
B4	0.46228	0.04602	0.36685
B5	0.49159	0.00209	0.47283
B6	0.38686	-0.05384	0.48544
T1	0.24322	-0.05515	0.39206
T2	0.19261	-0.02086	0.25271
T3	0.28183	0.03472	0.21913
T4	0.42167	0.05601	0.29918
T5	0.47227	0.02171	0.41281
T6	0.38305	-0.03386	0.44639
R1	0.07651	0.00423	0.05436
R2	0.21150	0.03270	0.13533
R3	0.26164	0.00324	0.25133
R4	0.17678	-0.05468	0.28635
R5	0.04179	-0.08314	0.20538
R6	-0.00835	-0.05369	0.08938
C20	0.24572	-0.02592	0.29482
C21	0.10526	-0.04961	0.21830
C22	0.05007	-0.01840	0.10305
C23	0.13535	0.03649	0.06431
C24	0.27581	0.06018	0.14083
C25	0.33100	0.02897	0.25609

APPENDIX D

Explanation of Space Group Labels

Table 22

Symbols for symmetry elements and for the corresponding symmetry operations in one-, two-, and three-dimensions [reproduced from (16)]

Printed symbol	Symmetry element and its orientation	Generating symmetry operation with glide or screw vector
m	Reflection plane, mirror plane	Reflection through a plane
	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 $\perp[\bar{1}\bar{1}0]$	$\frac{1}{2}\mathbf{c}$ }
	$\perp[1\bar{1}0]$ 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
	n-fold rotation axis, n	Counter-clockwise rotation of $360/n$ degrees around an axis
2,3,4,6	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

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	$\begin{cases} 0,0,0;\frac{2}{3},\frac{1}{3},\frac{1}{3};\frac{1}{3},\frac{2}{3},\frac{2}{3}\ (\text{'obverse setting'}) \\ 0,0,0;\frac{1}{3},\frac{2}{3},\frac{1}{3};\frac{2}{3},\frac{1}{3},\frac{2}{3}\ (\text{'reverse setting'}) \end{cases}$
	Primitive (description with 'rhombohedral axes')	1	$0,0,0$
H	Hexagonally centred	3	$0,0,0;\frac{2}{3},\frac{1}{3},0;\frac{1}{3},\frac{2}{3},0$

DATE	ISSUED TO