Separate aromatic compounds by forming adducts with thiourea : how to select the inductor
by Rebecca Lucille Welling

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE
in Chemical Engineering
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Abstract:
This thesis constitutes a framework from which a compound may be selected that is capable of inducing aromatic compounds into forming adducts with thiourea.

An aromatic compound which will form an adduct with thiourea without the presence of an inductor was discovered by the author.

This discovery led to the development of a new theory on hydrogen bonding.

This theory consists of a weak hydrogen bond contact between a methyl group in 1,2,4-trimethylbenzene and a sulfur atom in thiourea. Also, a hydrogen bond contact was recognized between a chlorine atom in the isomers of trichlorobenzene and an N-H group in thiourea.

A crystallographic structure analysis was completed for the adduct containing 1,2,4-trimethylbenzene. The results from this analysis support the theory on hydrogen bonding which was introduced by the author.

Two distinct requirements were recognized as necessary conditions for a compound which is capable of inducing aromatic compounds into forming adducts with thiourea. An inductor must possess the ability to (1) either induce hydrogen bonding through the sulfur atom in thiourea or to accept hydrogen bonding through the N-H group, and (2) geometrically accommodate the aromatic compounds within the channels that are formed through the hydrogen bond contacts.

Included in this thesis is a summary of the crystallographic data for the adduct containing 1,2,4-trimethylbenzene. Also included are recommendations for future research which will enhance the understanding of the mechanisms for the process of adduct-formation.

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Rebecca Lucille Welling

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ABSTRACT

This thesis constitutes a framework from which a compound may be selected that is capable of inducing aromatic compounds into forming adducts with thiourea.

An aromatic compound which will form an adduct with thiourea without the presence of an inductor was discovered by the author. This discovery led to the development of a new theory on hydrogen bonding.

This theory consists of a weak hydrogen bond contact between a methyl group in 1,2,4-trimethylbenzene and a sulfur atom in thiourea. Also, a hydrogen bond contact was recognized between a chlorine atom in the isomers of trichlorobenzene and an N-H group in thiourea.

A crystallographic structure analysis was completed for the adduct containing 1,2,4-trimethylbenzene. The results from this analysis support the theory on hydrogen bonding which was introduced by the author.

Two distinct requirements were recognized as necessary conditions for a compound which is capable of inducing aromatic compounds into forming adducts with thiourea. An inductor must possess the ability to (1) either induce hydrogen bonding through the sulfur atom in thiourea or to accept hydrogen bonding through the N-H group, and (2) geometrically accommodate the aromatic compounds within the channels that are formed through the hydrogen bond contacts.

Included in this thesis is a summary of the crystallographic data for the adduct containing 1,2,4-trimethylbenzene. Also included are recommendations for future research which will enhance the understanding of the mechanisms for the process of adduct-formation.

INTRODUCTION

Background

Mixtures of aromatic hydrocarbons occur frequently in cracking and refining processes of crude oil, and also in numerous synthetic processes. Because the compounds in these mixtures often have nearly identical properties, the separation and purification of these compounds is often difficult, costly and time consuming.

The field of separation is multifarious; and useful and novel techniques are in high demand. Due to the increasing costs of energy, there are current methods of separation for specific systems which may become economically obsolete. These are hard-to-separate systems which typically require large amounts of energy to effect a minimal degree of separation.

Extractive crystallization is a selective process wherein a given compound preferentially forms an adduct with the component desired from the separation. This process is a method of separating classes of hydrocarbons as well as separating specific isomers of a given empirical formula.

An adduct is the crystal formed when one compound surrounds other distinct compounds, trapping them within the channel or cage-like structure which is formed by this interaction.

The techniques of extractive crystallization have been applied to systems composed of straight chained hydrocarbons as well as to branched and cyclic hydrocarbons. In particular, urea will form an adduct with normal hydrocarbons[27] and thiourea will form a similar adduct with branched and cyclic hydrocarbons.[2]

Example:

> If a mixture of aliphatic compounds is brought into contact with urea dissolved in methanol, the normal paraffin material will be selected and crystallized from solution. If in place of urea, the same mixture is brought into contact with thiourea, the adducts formed will contain the branched and cyclic groups, separating them from the n-paraffins.

Extractive crystallization can be extended to an aromatic system by adding an ulterior compound to the aromatic mixture before the solution is brought into contact with thiourea. This ulterior compound induces the formation of adducts with aromatic compounds.

In general, aromatic compounds will not form adducts without the presence of this special compound.* The ulterior compound is

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*An exception was discovered by the author and is presented in this text.

referred to as an inductor. This inductor can be so specific that the right choice of inductor will readily distinguish between isomers.

McCandless[1,8,55] has shown that aromatic mixtures are effectively separated by induced extractive crystallization. He also indicated that the interaction between the inductor, the aromatic and the thiourea channel are not understood and, because of this, the method of selecting an inductor has been arbitrary.

Induced extractive crystallization is particularly attractive because it can be applied to hard-to-separate systems.* An understanding of the physical interactions among the components of the adduct will aid in the development of this separation technique on a commercial scale.

Thesis Inquiry

What procedure would provide a logical basis for gaining an understanding of the interactions between the inductor and the aromatic compound and between the inductor and the thiourea channel?

Are there particular substituents on a benzene ring which would allow an adduct to form?

What is the interactive role between substituents on a benzene ring and the thiourea channel? How can an understanding of this

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*Appendix II contains a discussion which illustrates industrial applications for induced extractive crystallization.

interaction be used to predict a suitable inductor for an aromatic system?

Specifically, how does the physical arrangement of atoms in the adduct relate to the extent of separation for an aromatic mixture?

Proposal

A crystallographic structure determination of an adduct provided an atomic view of this structure, thus establishing the relative positions among atoms and molecules in the adduct. This internal view provided a logical basis for gaining an understanding of the function of an inductor in the formation of an adduct containing aromatic compounds.

The idea was introduced in this text which suggests that the presence of certain substituents on a benzene ring not only allows the formation of an adduct, but encourages this formation as well.

Experimental evidence, together with a crystallographic structure analysis of a particular adduct, provided insight into the interactive role between a substituent on a benzene ring and the thiourea channel. The interactive role was theorized to be hydrogen bonding effects between the inductor and the thiourea.

Based on the hydrogen bond theories, certain conclusions were drawn which show a relationship between the atomic arrangement of the adduct and the selectivity of certain compounds in a mixture.

The investigation described in this text provided a foundation from which future studies may be constructed.

Purpose

Crystallographic structure studies on adducts formed with thiourea containing aromatic compounds have either not been completed or were not available in the literature. This thesis report has provided this information for future reference. In particular, the purpose of this crystallographic study was (1) to determine the dimensions of the channel for an adduct containing an aromatic compound, (2) to locate the atomic positions both of the aromatic isomer and of the inductor in the channel, (3) to provide a possible explanation regarding the role of an inductor in the formation of adducts containing aromatic hydrocarbons, and (4) to present concrete ideas for future investigations which would either support or refute the above explanation concerning the interactive function of an inductor.

Adducts for Structure Study

Initially, a crystallographic structure study was performed on an adduct which was known to be formed preferentially from a mixture of isomers of trimethylbenzene. The structure study was applied to the adduct containing 1,2,3-trichlorobenzene and 1,2,4-trimethylbenzene. This adduct was selected from Table I produced by F. P. McCandless.[8] Due to the apparent disorder of this

TABLE I

SEPARATION OF THE TRIMETHYLBENZENES USING TRICHLOROBENZENES AS INDUCTORS[a]

System	Inductor	Selectivity	α	ξ
hemimellitene (1,2,3) pseudocumene (1,2,4)	1,2,3 TCB	pseudocumene (1,2,4)	3.8	0.31
hemimellitene (1,2,3) pseudocumene (1,2,4)	1,2,4 TCB	pseudocumene (1,2,4)	1.8	0.15
hemimellitene (1,2,3) pseudocumene (1,2,4)	1,3,5 TCB	pseudocumene (1,2,4)	2.5	0.22
hemimellitene (1,2,3) mesitylene (1,3,5)	1,2,3 TCB	hemimellitene (1,2,3)	17.5	0.05
hemimellitene (1,2,3) mesitylene (1,3,5)	1,2,4 TCB	hemimellitene (1,2,3)	165.4	0.56
hemimellitene (1,2,3) mesitylene (1,3,5)	1,3,5 TCB	mesitylene (1,3,5)	12.7	0.07
pseudocumene (1,2,4) mesitylene (1,3,5)	1,2,3 TCB	pseudocumene (1,2,4)	178.3	0.59
pseudocumene (1,2,4) mesitylene (1,3,5)	1,2,4 TCB	pseudocumene (1,2,4)	708.0	0.64
pseudocumene (1,2,4) mesitylene (1,3,5)	1,3,5 TCB	mesitylene (1,3,5)	4.6	0.04
mesitylene o-ethyltoluene	1,3,5 TCB	mesitylene	9.3	0.15

(a) All feed solutions approximately 50% of each isomer

adduct, samples were sent to Molecular Structure Corporation for a structure analysis. Molecular Structure Corporation encountered the same problems of disorder, and so a sample of a different adduct was sent for analysis. This adduct contained only 1,2,4-trimethylbenzene. Although the structure of this adduct was also disordered, a solution was obtained. The results of this atomic analysis provided support for the new theory on hydrogen bonding which is presented in this text.

Elementary Crystallography

A basic description of the procedures which are applied in a crystallographic structure study was not available in the literature; the literature findings were complex and required an in-depth review in order to summarize the essential requirements for a structure study. For this reason a brief and elementary discussion is included in this thesis report; however, the review is not an integral part of this thesis and was, therefore, placed in Appendix VI.

Historical Review

Extractive crystallization has been employed as a separation process on a commercial scale.[20,41,42,43] The primary application was the dewaxing of middle and heavy distillates using urea to form adducts with the straight chained hydrocarbons. Marechal and Radzitzky[18] provided a good discussion of laboratory investigations wherein urea was used as a dewaxing agent.

An article by Fetterly[41] included a review of important pilot plant studies of the dewaxing process using urea, as well as a discussion which provides information on the location and operation of several commercial units for this process. One of these commercial units was constructed in 1956 in Whiting, Indiana by Amoco Oil Company. The economics of this process after plant start-up were more favorable than were the initial projections for this unit. The pilot plant tests for this particular unit as a batch process were successful, but the technique was never tested as a continuous process. The major problem for the commercial unit was that of recovering the urea from the process so that it could be recycled. This problem was believed to be surmountable; however, more laboratory work was required. The operation of this unit was discontinued in the sixties, but the closure of the unit for this operation was not attributed solely to process difficulties.[40]

The ability of thiourea to form adducts with branch chained and cyclic hydrocarbons was disclosed by Fetterly.[2] Further studies were reported by Redlich[5] and in his report he included composition and equilibrium constants for several adducts as well as approximate activity values for these adducts.

Lenne[56] completed crystallographic structure studies of thiourea-hydrocarbon adducts. His report was thorough and included complete data for the structure determination of the adduct

containing cyclohexane. He stated that the basic geometry of these adducts was constant, and that thiourea comprised the outer shell of the channel. The adducts were rhombohedral with space group $R\bar{3}2/c\text{-}D_{3d}^{6}$.

Smith[6,7] performed x-ray analyses for several adducts containing branch chained hydrocarbons which were formed with thiourea. He reported that in general the unit cell was rhombohedral, but he noted a few exceptions to this classification which suggested an orthorhombic unit cell.

McLaughlin[37] also noted a discrepancy among authors concerning the structure of adducts containing branched and cyclic hydrocarbons which were formed with thiourea. This disagreement was attributed to the "low" stability of these adducts. In his report, McLaughlin included lists of composition data for several adducts and provided a comparison of the relative ability of certain compounds to form adducts. He also provided the data from x-ray diffraction studies for some of these adducts.

The information and ideas proposed in this thesis report have shown that the discrepancies reported in the literature concerning the structure of adducts with thiourea need not be a disagreement, but may represent true findings; crystal structures of adducts formed with thiourea can vary.

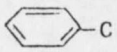
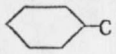
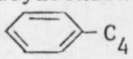
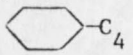
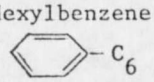
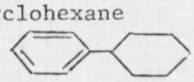
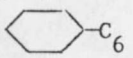
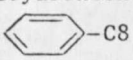
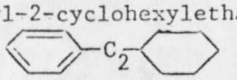
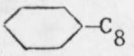
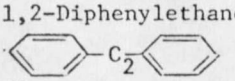
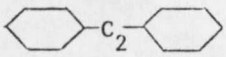
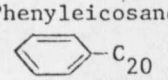
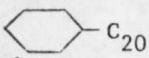
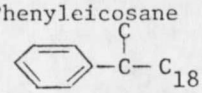
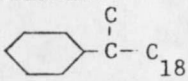
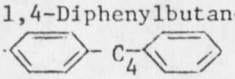
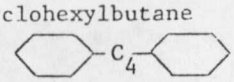
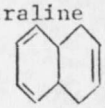
McLaughlin[37] reported a channel size of approximately 6.8 Å by 5.6 Å for the adducts formed with thiourea and which contain branched and cyclic hydrocarbons. Included in this treatise was the concept of aromatic compounds which will not form adducts with thiourea, but which possess the proper channel size to allow the formation of the adduct. A good comparison of compounds which will form adducts to compounds which will not form adducts, but which have the same relative size, is shown in Table II, page 11. Whether an actual structure study was completed for those compounds in Table II which did form adducts with thiourea was unclear. This report also included heat of formation data for several adducts.

X-ray studies were completed by Stein and Allock[12,29] on "clathration" compounds used to separate hydrocarbons. Although the separation process which was employed to form these "clathration" compounds was that of extractive crystallization, neither urea or thiourea was used as the compound which forms the outer structure of the adduct. Similar work was performed by Siegel[15,16] and co-workers.

The separation of aromatic compounds by extractive crystallization was explored by Radzitzky[3] and Schaeffer[4,22,25] using Werner Complexes. The formation of these complexes did not involve either urea or thiourea.

TABLE II

COMPOUNDS WHICH FORM ADDUCTS WITH THIOUREA VERSUS COMPOUNDS WHICH DO NOT

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

*Reproduced from McLaughlin[37]

McCandless[1,8,55] has shown that aromatic compounds can be induced to form adducts with thiourea, and that this process can be used as an effective separation technique for hydrocarbon systems.

An exception has been determined by the author of an aromatic compound which will form an adduct without an inductor present. A discussion of this compound is presented in this text. The ability of this aromatic compound to form an adduct is attributed to special geometry as well as to slight hydrogen bonding effects between the methyl groups attached to the benzene ring and the sulfur atoms in thiourea.

Crystallographic structure studies were not available in the literature concerning adducts that are formed by the entrapment of both an aromatic compound and an inductor by the thiourea-channel. Two crystallographic structure analyses are discussed in this text. One is a complete structure determination and the other is only partially complete.

EXPERIMENTAL

A summary of the data which corresponds to the experimental work that is described in this section is presented in Table III and Table IV.

Thiourea Adduct Studies

Experiments were performed to determine whether or not certain compounds would individually form adducts with thiourea. The isomers of trimethylbenzene and the isomers of trichlorobenzene were the compounds for which these experiments were completed. The results are shown in Table IV.

In each case, 12.5 g of thiourea was dissolved in 25 ml of methanol by applying heat. At the boiling point of this mixture, 10 ml of isomer was added. This slurry was immediately placed in an ice chest at -17° C and left for seventy-two hours.

Crystal Preparation

Since large and well-formed crystals are required to produce satisfactory x-ray diffraction data, various methods of crystal growth were investigated.* A suitable crystal was obtained by prudent selection of adducts which were prepared in the manner described by McCandless.[8,55] This method is described in the following paragraph.

*Appendix III contains a summary of the methods which were employed for crystal growth.

TABLE III

GENERAL CRYSTAL DATA

Adducts Containing	Density (g/ml)	Melting Point	Space Group	Empirical Formula
1,2,3,-trichlorobenzene 1,2,4-trimethylbenzene	1.27	178 C	$P2_1/c$	$C_{32}H_{66}N_{18}S_9Cl_4$
1,2,4-trichlorobenzene 1,2,3,-trimethylbenzene	1.3		$P2_1/c$	$C_8H_{16}N_6S_3Cl_2$
1,2,4-trichlorobenzene 1,2,4,-trimethylbenzene	1.3	178 C	$P2_1/c$	$C_6H_{12}N_4S_2Cl$

TABLE IV

COMPOUNDS TESTED FOR ADDUCTABILITY

COMPOUND	ADDUCTABILITY
1,2,3-trichlorobenzene	adducting
1,2,4-trichlorobenzene	adducting
1,3,5-trichlorobenzene	adducting
1,2,3-trimethylbenzene	nonadducting
1,2,4-trimethylbenzene	adducting
1,3,5-trimethylbenzene	nonadducting

In general, thiourea was dissolved in methanol by heating and combined with a mixture of hydrocarbons and the inductor. Although the formation of adducts occurs on contact of these two solutions at standard conditions, the slurry was mixed and immediately placed in an ice chest at -17° C for twenty-four hours or more.

In all cases, the mass ratios of thiourea to methanol and of hydrocarbon to inductor were 1:2 and 1:3, respectively. The mass ratio of thiourea to hydrocarbon-inductor mixture was 1.25:1.

Adduct Density

The density of an adduct was determined by suspending the adduct in a mixture of miscible liquids, one more dense than the adduct and one less dense. The density of the solution which is in equilibrium with the adduct is also the density of the adduct.[33]

The solution densities were determined with a hydrometer. In each case, a medium composed of heptane and 1,2,4-trichlorobenzene was used. Measurements taken for five different solutions were averaged together for each adduct. The maximum experimental error which was allowed was four percent.

The empirical formula was determined for each adduct from the corresponding elemental analysis which was performed by Galbraith Laboratories in Knoxville, Tennessee. Knowledge of the density of the adduct as well as the knowledge of the empirical formula helped to establish the number of atoms per unit cell.

Appendix IV contains an example of these calculations.

Photographic Film Studies

Both Weissenburg and Buerger Precession cameras were used. Weissenburg photographs were collected for five different adducts. Data sets consisting of oscillation, zero level, first level and second level photographs were obtained.

Diffractometer

A complete data collection was obtained for the adduct containing both 1,2,3-trichlorobenzene and 1,2,4-trimethylbenzene. A General Electric XRD-6 Diffractometer equipped with a scintillation counter, pulse-height discriminator, and G.E. single crystal orienter was employed. A θ-2θ scan technique was used along with zirconium-filtered molybdenum K-radiation. The data were collected and recorded on a PDP-11 computer.

Computer Analysis

Multan 76, a well-known direct methods computer program, was applied, as was a new version of X-Ray 76 obtained from Keith Watenpaugh from the University of Washington, and adapted to the new VAX/VMS computer at Montana State University. Multan 76 was produced by J. M. Stewart of the University of Maryland.

Appendix V contains a list of all the programs that were available with these computer packages.

Elemental Analysis

Galbraith Laboratories in Knoxville, Tennessee, completed an elemental analysis for each adduct. They proclaimed an error range of five-tenths of one percent.

The adducts required an atmosphere containing both the hydrocarbon and inductor to prevent deterioration. For this reason, the following method was devised to seal the samples in a container suitable for shipping.

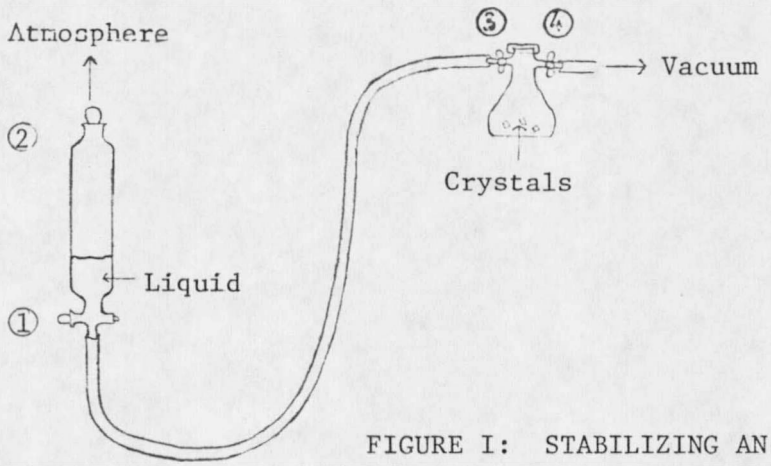


FIGURE I: STABILIZING AN ADDUCT

Procedure: (See Figure I)

1. Close valve 1, maintaining atmospheric pressure above the liquid.
2. Open valves 3 and 4. This establishes a vacuum in the flask containing the adducts and in the line to point 1.
3. Close valve 4.

4. Successively open valves 1 and 2. The equilibrium pressure is atmospheric and the atmosphere above the adducts contains the hydrocarbon-inductor mixture.

5. Close valve 3.

Molecular Structure Corporation

Molecular Structure Corporation in College Station, Texas, completed a structure determination for the adduct containing 1,2,4-trimethylbenzene. They also completed several data collections, including low temp data collections for the adduct containing both 1,2,3-trichlorobenzene and 1,2,4-trimethylbenzene.

A description of the experimental procedures which were employed by Molecular Structure Corporation for the solution of the structure is contained in Appendix VII. This description was taken directly from their structural report.

RESULTS AND DISCUSSION

Adducts Containing Aromatic Compounds

Although it has been accepted that aromatic compounds generally do not form adducts with thiourea without the presence of an inductor, the compound 1,2,4-trimethylbenzene was employed as an inductor for an ethyltoluene system.[17] The results of this experiment prompted further investigation by the author. Because 1,2,4-trimethylbenzene successfully induced the formation of adducts for the ethyltoluene system, it was predicted that the aromatic compound itself would form an adduct with thiourea. Experimental results proved that this prediction was accurate and 1,2,4-trimethylbenzene was discovered to form an adduct with thiourea without the presence of an inductor.

Experiments were performed which tested all of the isomers of trimethylbenzene and all of the isomers of trichlorobenzene to determine which compounds would form adducts with thiourea. The formation of an adduct containing 1,2,4-trimethylbenzene was noted above. The other two isomers, 1,2,3-trimethylbenzene and 1,3,5-trimethylbenzene, did not form adducts with thiourea. All three isomers of the trichlorobenzene system did form adducts with thiourea.

These experimental results are the basis for the ideas on hydrogen bonding which are theorized to be responsible for the formation of adducts which include aromatic compounds. The information

obtained from Molecular Structure Corporation support these ideas.

Before any samples of adducts were sent to Molecular Structure Corporation for analysis, several attempts were made by the author to solve the structure of the adduct containing both 1,2,3-trichlorobenzene and 1,2,4-trimethylbenzene.

Preliminaries

A complete data collection from the diffractometer was obtained for the adduct containing 1,2,3-trichlorobenzene and 1,2,4-trimethylbenzene. Normally, a time period of about two or three days is typical for a data collection, but problems were encountered involving the stability of the adduct. The adducts were found to deteriorate if (1) the environment of the adduct was open to the atmosphere for more than one hour, and (2) the adduct remained in an open atmosphere when it was brought into contact with a continuous x-ray beam.

The problems of stability were surmounted by encapsulating a single adduct in a glass capillary tube and establishing equilibrium between the adduct and the vapor from the corresponding mixture of hydrocarbon and inductor.

Macroscopically, the adducts were colorless, transparent, long needle-like structures. An adduct with a thickness of one to two millimeters provided the least distorted diffraction pattern. The

adduct was placed in a five millimeter capillary tube and the ends were sealed with wax.

The deterioration of an adduct was visually noted when the adduct became cloudy and subsequently turned white. Weissenburg photographs which were collected for the deteriorated adduct showed few, if any, layer lines and those lines which were present contained indefinite spots.

The outer frame of the adduct was expected to be comprised of thiourea and to be surrounding the aromatic isomer and inductor, thus trapping them inside. Weissenburg photographs which were collected for five different adducts supported this concept. These photographs indicated that the unit cell parameters were identical for all of the adducts which were considered; the photographs could be geometrically superimposed. This structural overview of the channel agrees with literature citings which refer to studies on adducts which were formed using urea and contained n-paraffins as well as with some studies for adducts which used thiourea and contained branched and cyclic compounds.[6,36]

The Weissenburg photographs for the adducts which are listed in Table III, page 14, indicated that these crystals belong to a monoclinic* crystal system. These photographs contained very few high intensity

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*Appendix I contains a list of the classifications of crystals.

reflections which implies that the physical arrangement on the interior of the channel is very likely disordered.

Numerous Buerger Precession photographs were taken for the adduct containing 1,2,3-trichlorobenzene and 1,2,4-trimethylbenzene. These photographs were expected to provide support for as well as clarification of the parameters which were determined based on the Weissenburg films. Problems were encountered which involved the alignment of the crystal for the precession photographs and this method was abandoned because these photographs were not necessary to proceed with a data collection from the diffractometer.

Data Collection

A complete data collection was obtained from the diffractometer for the adduct containing 1,2,3-trichlorobenzene and 1,2,4-trimethylbenzene. The adduct was mounted along an axis which was designated as the c axis. Measurements from Weissenburg photographs indicated that the approximate values for the unit cell parameters were a=9.8 A, b=15.3 A, c=12.64 A, $\beta=\gamma=90$ and $\alpha=113.85°$.

Three thousand three hundred and ninety-nine unique intensities were originally collected from the diffractometer. Of these 3399 intensities, only 1421 intensities were considered to correspond to observed reflections. A study of these intensities indicated the following extinctions:

Reflection	Absent	
h00	h=2n	
0k0	k=2n	030 weakly present
001	no conditions	
hk0	no conditions	
h01	no conditions	
0k1	k=2n	030 weakly present

A space group of $p2_1/b$ was determined by coordinating these extinctions with the symbols for symmetry elements taken from Table 6 in Buerger.[39] The space group was then translated to the standard of $P2_1/c$ and b became the unique axis, replacing c. This translation was accomplished by reference to The International Tables for X-Ray Crystallography and the translated parameters became a=12.64, b=15.3, c=9.8 A and β=113.85°. Both the space group and the parameters were supported by the data which was collected by Molecular Structure Corporation for the same adduct.

Computer Analysis

Appendix V contains a list of all the programs which were applied and which are mentioned in this section.

The original raw data were collected on a PDP-11 computer, producing a tape written in ebidic. This tape was translated into ascci which is required by the VAX/VMS computer.

Programs were first selected from X-Ray 76 to refine and analyze this data set. DATRDN edited the raw data and prepared a binary data file suitable for other programs. Several other programs were then applied. Difficulty was encountered and it was discovered that some of the programs were not linked to the main system.

At this point EVAL, SINVAR, GENTAN and PREMAP were considered. These programs were only partially successful. These complications were encountered because the programs were preliminary programs and not fully documented.

The data were next supplied to the programs which are listed in Multan 76. This system ran successfully, but problems were encountered due to the disorder of the adduct and the data failed to produce a satisfactory solution.

Structural information and the knowledge of basic composition which are determined prior to a diffraction study, should be evident from and correspond to the data which is collected from the diffractometer; if this data truly represents the structure of the adduct.

The adduct was known to be composed of molecules of thiourea, 1,2,3-trichlorobenzene and 1,2,4-trimethylbenzene. The relative proportions of these compounds in a unit cell had been determined earlier. Thiourea was expected to be attached to itself by hydrogen bond effects through S and N-H, thus forming a spiral which encloses the other two compounds.

The results from the program EXFFT did not reveal any related peaks which could be assigned to a known molecule. The highest peaks should have corresponded to sulfur and/or chlorine because they were the heaviest atoms present.

Following EXFFT, the program SEARCH located the positions of the highest peaks from EXFFT and searched for groups of peaks which could form a molecule. Because thiourea is sp_2-hybridized, if any of these fragments had corresponded to a thiourea structure, the angles would be approximately 120° and the bond lengths approximately 1.3 A. Although several variations of these programs were successfully run, the output did not reveal any phases which were worthwhile. The calculations of the structure factors from the atomic positions which were produced from Multan did not provide an R factor less than 0.60. The R factor is defined to be

$$R = \Sigma |F_o - F_c| / \Sigma |F_o| .$$

Where F_o is the observed structure factor, and
F_c^o is the calculated structure factor.

The overall analysis indicated that the crystal was disordered, and it became evident that considerably more time would be required to obtain a solution and that, in any event, success was not guaranteed for the solution of this adduct.

The main concern of this thesis was not the crystallographic structure study of an adduct, but rather the acquisition of crystallographic results and the application of these results to gain an

understanding of the formation of adducts using thiourea and which contain aromatic compounds. For this reason, samples of two distinct adducts were sent to Molecular Structure Corporation for analysis. One of these adducts contained both 1,2,3-trichlorobenzene and 1,2,4-trimethylbenzene and the other adduct contained only 1,2,4-trimethylbenzene.

The discovery of the adduct which contains only 1,2,4-trimethylbenzene led to a theory on hydrogen bonding between the sulfur atom in thiourea and the C-H group in 1,2,4-trimethylbenzene.

Molecular Structure Corporation

Although a complete structural solution was not obtained for the adduct containing both 1,2,3-trichlorobenzene and 1,2,4-trimethylbenzene, both the space group and the dimensional parameters were determined. The outcome of this analysis is in agreement with the results which were obtained by the author for the same adduct.

A solution was obtained by Molecular Structure Corporation for the structure of the adduct containing 1,2,4-trimethylbenzene. The details of the structural report are contained in Appendix VII. The space group for this adduct is $P2_1/c$ and the parameters are a=12.3 A, b=15.1 A, c=10.0 A and β=112.7°. The trimethylbenzene molecules have a disordered arrangement from a translational view as well as through the inversion centers.

The intermolecular contacts for this adduct are shown in Table XIV. This information was used to support some of the conclusions which were made regarding the hydrogen bond contacts in the adduct.

TABLE V

INTERMOLECULAR CONTACTS TO 4.ØØA

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
S1	C11	3.9Ø(3)	N4	C9	3.98(3)	N1	S2	3.35Ø(1Ø)
S1	C12	3.65(3)	N4	C1Ø	3.87(3)	N1	S2	3.433(11)
S1	C13	3.81(3)	N4	C11	3.95(3)	N1	C2	3.93(2)
C1	C6	3.82(3)	C3	C9	3.95(3)	N1	N3	3.678(14)
N1	C4	3.54(3)	N5	C9	3.84(3)	S2	N6	3.4Ø8(1Ø)
N1	C5	3.6Ø(4)	N5	C9	3.64(3)	N3	N3	3.97(2)
N1	C6	3.74(3)	N5	C1Ø	3.55(3)	N4	S3	3.422(1Ø)
N1	C13	3.93(3)	N5	C1Ø	3.74(3)	N4	S3	3.349(1Ø)
N2	C6	3.87(3)	N5	C11	3.98(3)	S3	N5	3.372(11)
N2	C7	3.98(4)	N6	C11	3.9Ø(3)	S1	N5	3.392(11)
S2	C13	3.91(3)	N6	C12	3.89(3)	N2	S3	3.444(1Ø)
C2	C6	3.87(3)	S1	N2	3.369(1Ø)	N2	N5	3.89Ø(14)
N3	C4	3.67(3)	S1	N3	3.424(1Ø)	S2	N6	3.38Ø(1Ø)
N3	C5	3.91(3)	S1	N3	3.354(1Ø)	C2	N6	3.939(15)
N3	C13	3.8Ø(3)	C1	N3	3.92(2)			
N4	C6	3.95(3)	C1	N3	3.99Ø(15)			

Numbers in parentheses are estimated standard deviations in the least significant digits.

CONCLUSIONS

Literature citings were referred to earlier which substantiated several important concepts concerning the formation of adducts with urea and thiourea: Both urea and thiourea form hydrogen bonds with themselves, thus creating a spiral which can trap hydrocarbons. The adducts that are formed have a crystalline structure which is different from either pure urea or pure thiourea. Because sulfur is a larger atom than oxygen, the channel dimensions for the adducts that are formed with thiourea are larger than those that are formed with urea.

The straight chained hydrocarbons which accommodate the channels formed by urea are too small to become trapped within a channel formed by thiourea. The phenomena are explained by a simple lock-and-key effect; and there is no evidence which would indicate hydrogen bond interactions between the hydrocarbons and either urea or thiourea.* In general, aromatic hydrocarbons do not form adducts with thiourea; in particular, those aromatic compounds which have the same relative size as their cyclic compound counterparts will not form adducts.

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*McLaughlin[37] and Brook[36] refer to a "supported hydrogen bond" concept.

Table II, page 11, compares aromatic compounds that will not form adducts with thiourea with the cyclic compounds of the same relative size which will form adducts. To explain the behavior of the aromatic compounds in this table, consider benzene versus cyclohexane.

Although benzene is a flat compound and cyclohexane has both chair and boat configurations, the diameter of the channel for the adduct is the appropriate size which should accommodate both compounds. Because the isomers of trichlorobenzene are planar compounds and these isomers do form adducts with thiourea, it is unlikely that the planar configuration of benzene is wholly responsible for preventing the formation of an adduct. However, benzene and cyclohexane have different electronic configurations.

Both the sulfur atom and nitrogen atoms in thiourea contain lone pairs of electrons. The structure of benzene consists of pi clouds which lie both above and below the plane of the carbon atoms. By recognizing these facts, the interaction between benzene and thiourea can be explained as a repulsive force between the electron pairs on both nitrogen and sulfur and the pi clouds around benzene. This repulsive force is greater than the spiraling tendency of thiourea which is caused by hydrogen bond contacts between thiourea molecules; this repulsive force interferes with the formation of channels by thiourea.

Although benzene will not form an adduct with thiourea, the isomers of trichlorobenzene will form adducts. Because of these

facts, the presence of the chlorine atoms on the benzene ring must be responsible for this formation.

Chlorine is an electronegative atom and it is recognized as a hydrogen bond acceptor.[52,53] 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.

The isomers of trichlorobenzene are able to induce other aromatic compounds into forming adducts with thiourea. This is because the geometry formed by the interaction of the trichlorobenzene with thiourea is able to accommodate and trap the compounds which are being induced.

The fact that 1,2,4-trimethylbenzene will form an adduct with thiourea, but the other two isomers of trimethylbenzene will not form adducts, leads to speculation which introduces a new type of hydrogen bond. The methyl groups which are attached to the benzene ring must be responsible for the formation of the adduct. The benzene ring increases the electron density of the carbon atom on a methyl group.* This methyl group becomes slightly acidic through this resonance effect and will induce weak hydrogen bonding with the sulfur atom in thiourea. The methyl groups are dispersed around the benzene ring

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*This concept on hydrogen bonding was introduced by John Cardellina, professor of chemistry at Montana State University, in a private discussion with the author.

in a fashion which creates the appropriate geometry, and through hydrogen bonding are able to anchor the 1,2,4-trimethylbenzene within the channel.

If a hydrogen bond contact exists between a C-H group and S, then the observed distance must be less than the nonbonded distance which would be expected under normal circumstances.

The nonbonded distance is calculated:

nonbonded distance[54] = 4.08A = covalent radii for C-H group, 1.08 A
+ Van der Waals radii for H, 1.15 A
+ Van der Waals radii for S, 1.85 A

The observed contacts between sulfur and carbon which were determined by Molecular Structure Corporation are listed in Table V, page 29. These distances are summarized:

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

All of these observed contacts are less than the expected nonbonded distance, 4.08 A; in particular, the distance between S1 and C12 is 3.65 A (about 11% less). This difference is significant and indicates that an attractive force exists between these molecules and may be explained as a hydrogen bond interaction.

The methyl groups on 1,3,5-trimethylbenzene are symmetrically dispersed about the benzene ring and the methyl groups on

1,2,3-trimethylbenzene are concentrated to one side of the ring. The fact that 1,2,4-trimethylbenzene did form an adduct with thiourea and both 1,3,5-trimethylbenzene and 1,2,3-trimethylbenzene did not form adducts, must be attributed to the relative size of these isomers with respect to the dimensions of the thiourea-channel. Both 1,3,5-trimethylbenzene and 1,2,3-trimethylbenzene are larger than this channel size.

The occurrence of adducts containing aromatic compounds creates a framework from which new ideas regarding intermolecular attractions may be studied. This framework is available because stronger attractive forces are required to form adducts containing aromatic compounds compared to the weaker attractive forces which form adducts containing aliphatic compounds. Before the adducts containing aromatic compounds were recognized, Mandelcorn[36] was aware that an unusual driving force aided in the formation of adducts.

> "An important point that is easily overlooked when considering the stabilizing forces of inclusion complexes (adducts) of both the cage and channel types is that we have for the first time evidence of a new concept that a stronger hydrogen bond can exist only when it is supported by an otherwise inert surface capable of exerting only weak dispersion forces. Prior to the studies made on inclusion complexes, this new driving force was unrecognized. Without the support of a paraffin, inert gas, or other fairly nonreactive molecules, such substances as gas hydrates, urea, and thiourea complexes, and several other inclusion complexes just cannot exist."[36]

This "supported hydrogen bond" concept was also referred to by McLaughlin;[37] the idea deserves further investigation. The lock-and-

key phenomena is a stabilizing factor for the adducts, but it does not necessarily follow that a "support" for hydrogen bonding exists in the sense that the strength of the hydrogen bond itself is actually increased.

Thiourea is unable to form an adduct with straight chained hydrocarbons. This fact, together, with other information concerning the formation of adducts, indicates that both stabilizing forces are necessary. The fact that these forces are distinct from each other becomes more clear when adducts containing aromatic compounds are investigated.

Before aromatic compounds will form adducts, they must be induced. An inductor must be capable of either inducing hydrogen bonding through the sulfur atom on thiourea or accepting hydrogen bonding through the N-H group. As in the case of 1,2,4-trimethyl-benzene, a compound which induces hydrogen bonding through the sulfur atom will have more geometric restraints than the compound which can induce hydrogen bonding through the N-H group. This is largely due to the fact that the availability of sulfur to nitrogen is 2:1.

A compound is termed an "inductor" because it has the ability to both select and trap a particular hydrocarbon in the channels it forms with thiourea. This ability depends mostly upon the geometry of the channels and the geometry of the corresponding hydrocarbon.

Flitter and Schiessler[10] reported that the average channel size for adducts formed with thiourea and containing branched and cyclic compounds is 5.8 A by 6.8 A. The channel dimensions for the structure of the adduct discussed in this text are approximately 9.6 A by 6.4 A. These are center-to-center distances; the distances were not adjusted to account for the size of the atoms. Correcting for Van der Waals packing, these dimensions reduce to about 5.9 A by 3.4 A. This would be the channel size if no attractive forces existed between the methyl groups on 1,2,4-trimethylbenzene and the sulfur atom in thiourea. The dimension 9.6 A corresponds to the length of the channel which lies in the plane of the carbon atoms on 1,2,4-trimethylbenzene. Because the smallest dimension of 1,2,4-trimethylbenzene is about 6.2 A, the actual channel length in the carbon plane must be between 6.2 A and 9.4 A. This larger channel size, which represents the aromatic compounds, indicates that thiourea is able to accommodate a wide range of compounds (inductors). The flexibility of the structure of the adduct is an important consideration when an inductor is selected for a given system.

A compound which serves as an inductor for an aromatic system must be able to form an adduct with thiourea. This occurs when the inductor forms hydrogen bond contacts through either the sulfur atom on thiourea or one of the nitrogen atoms. The net effect of this driving force creates special geometric patterns which can be manipu-

lated by the selection of the inductor. The specificity of this separation technique is a powerful tool. The process shows strong application for hard-to-separate systems and is attractive for commercial development.

RECOMMENDATIONS

Aromatic compounds can be effectively separated by a crystallization technique that uses thiourea and is termed Induced Extractive Crystallization. Both the selectivity of a hydrocarbon from a mixture and the degree of separation of that mixture are governed by the inductor which is employed.

Up until this time, the selection of an inductor for a particular system has been arbitrary. The content of this thesis report has provided insight into the "inducing" characteristics of an inductor.

Urea has been used commercially to separate broad classes of compounds. This separation technique can be applied to hard-to-separate systems using thiourea with the appropriate inductor. There are several important systems which economically are becoming more and more difficult to separate. This process should be developed; all aspects of the process require research. The recommendations which are included are only those which are directly related to the thesis material.

A direct extension of this thesis would include a crystallographic structure study of at least two different adducts. One adduct should contain only an isomer of trichlorobenzene, such as 1,2,4-trichlorobenzene. The other adduct should contain both an isomer of trichlorobenzene and an isomer of trimethylbenzene

(not 1,2,4-trimethylbenzene). A good choice is the adduct containing 1,2,4-trichlorobenzene and 1,2,3-trimethylbenzene.

Structural studies of these adducts would either verify or refute the hydrogen bond theory regarding a chlorine atom with an N-H group in thiourea. The same inductor should be used in both adducts. This will provide interesting comparisons for the channels which are formed by the interaction of the inductor with thiourea. This will also provide important information regarding the orientation of the hydrocarbon within the channels.

McCandless[8] discovered that the inductor carbon tetrachloride favors cumene, n-propylbenzene and indan from the reformate shown in Table VI, page 40. These compounds are not as large as the compounds involved in the trimethylbenzene-trichlorobenzene system. Therefore, a crystallographic structure study of an adduct from this system may result in a different crystal classification.

McLaughlin[37] reported that tert-butylbenzene forms an adduct with thiourea in the absence of an inductor. It would be difficult to try and explain this formation by any hydrogen bond theories. However, it is quite plausible that the tert-butyl group is able to lock into the channel formed by thiourea. This view would place the phenyl group sticking out of the spiral. A structure study of this compound would clarify this arrangement. This structure can be anticipated to be rhombohedral, corresponding to the structure for

TABLE VI

APPROXIMATE COMPOSITION AND NORMAL BOILING POINTS OF ALKYLBENZENES IN C_9 REFORMATE

Compound	Approximate Composition, Wt.% (Love and Pfennig, 1951)	Normal B.P., °C (Weast, 1976)
cumene (isopropylbenzene)	0.4	152.4
n-propylbenzene	5.7	159.2
m-ethyltoluene	21.0	161.3
p-ethyltoluene	9.6	162.0
mesitylene (1,3,5 trimethylbenzene)	9.3	164.7
o-ethyltoluene	9.0	165.2
pseudocumene (1,2,4 trimethylbenzene)	34.8	169.3
hemimellitene (1,2,3 trimethylbenzene)	8.5	176.1
indan	1.7	178.0

branched and cyclic compounds. If the structure containing tert-butylbenzene happened to be different from the rhombohedral structure; if the unit cell parameters are larger than those for branched compounds, then tert-butylbenzene would be a good candidate as an inductor for an aromatic system. This line of thought applies to all compounds listed in Table II, page 11, which form adducts, but also contain phenyl groups.

A physical model of an adduct would be a very beneficial tool. In particular, a model of the adduct containing 1,2,4-trimethylbenzene should be constructed. This chore would provide necessary information regarding the geometry of these channels. Modeling Chemical Structures, by McClellan[54] and MacNab, includes a very thorough description of several methods for chemical modeling.

SUMMARY

Induced extractive crystallization is a novel separations technique which effectively separates systems composed of aromatic compounds. In this process, thiourea spirals around a special compound (inductor) by forming hydrogen bond contacts. This creates channels which can trap aromatic compounds inside. A unique crystalline structure (adduct) is formed. The aromatic compound is then recovered from the adduct by conventional methods such as steam stripping, followed by phase separation of the products.

This dissertation provided a framework from which an inductor for a particular system can be selected in a logical manner. This framework consists of the principles which typically prevent an aromatic compound from forming an adduct with thiourea, but allow this adduct to form in the presence of an inductor.

The aromatic compound, 1,2,4-trimethylbenzene, was discovered by the author to form an adduct with thiourea in the absence of an inductor. This provided insight into the characteristics that are required for a compound to function as an inductor. This also introduced ideas regarding the intermolecular activities for the overall process of adduct-formation.

A rationale was reached which is the basis for selecting an inductor. An inductor must possess the ability to (1) either induce

hydrogen bonding through the sulfur atom on thiourea or to accept hydrogen bonding through the N-H group, and (2) geometrically accommodate the aromatic compounds within the channels that are formed through the hydrogen bond contacts.

Adducts which contain aromatic compounds can be formed with thiourea. The recognition of this occurrence is important for two distinct reasons which are outlined in the following paragraphs.

First, this phenomenon introduces an attractive new separations technique for hard-to-separate systems; systems that are difficult to separate by conventional methods. This is evident because the technique can be applied to those systems which are difficult to separate by conventional methods. This thesis contains recommendations for future research which will aid in the development of this technology.

The second reason this phenomenon is important is because it becomes a framework from which new concepts on intermolecular forces can be further investigated. A new hydrogen bond contact was observed by the author between a methyl group in 1,2,4-trimethylbenzene and a sulfur atom in thiourea. This observation was supported by a complete crystallographic structure analysis for the adduct containing this isomer. In addition, there is historical recognition of the need for a special driving force for the overall formation of adducts containing aliphatic compounds. These two independent observations

indicate that adduct-formation, in general, constitutes a prime source for novel scientific investigations concerning intermolecular activity.

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APPENDICES

APPENDIX I--CLASSIFICATION OF CRYSTALS

There are seven three-dimensional coordinate systems which are used to classify crystals.[33] In general, the unit cell is characterized by a certain symmetry and six parameters, three axial lengths and three interaxial angles. The lengths of the unit cell edges are designated a, b, c and the interaxial angles α, β, γ where α is the angle between b and c, β is the angle between a and c, and γ is between a and b.

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

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

APPENDIX II--RELATED RESEARCH EFFORTS AT MONTANA STATE UNIVERSITY

The following discussion briefly summarizes research efforts completed by F. P. McCandless and co-workers at Montana State University. The results of these findings clearly indicate the usefulness of induced extractive crystallization as a novel separation technique. The implications of these findings are the motivation for the research described in this text.

There are numerous industrial processes which require a particular isomer in relatively high purity. The following list illustrates a few of these compounds as well as their uses.[34]

COMPOUND	USE
1,2,4-trimethylbenzene	Manufacture of trimellitic anhydride, dyes, pharmaceuticals and pseudocumidine
1,3,5-trimethylbenzene (mesitylene)	Intermediate; ultraviolet oxidation stabilizers for plastics
Meta-xylene	Solvent; intermediate for dyes and organic synthesis; insecticides, aviation fuel
Ortho-xylene	Manufacture of phthalic anhydride; vitamin and pharmaceutical syntheses; dyes; insecticides
Para-xylene	Synthesis of terephthalic acid for polyester resins and fibers (Dacron, Mylan, Terylene); vitamin and pharmaceutical syntheses; insecticides

Ethylbenzene	Intermediate in production of styrene solvent; the 20th highest volume chemical produced in U.S. in 1975.
Isopropylbenzene (cumene)	Production of phenol, acetone, and alpha-methylstyrene; solvent
Indan	Organic synthesis

Some of these compounds are shown in Table VI, page 40, as they occur in reformate along with their corresponding boiling points.

Several compounds exhibit physical and chemical properties of similar proportion. Techniques such as distillation and solvent extraction rely on a difference in these properties to effect the separation. Extractive crystallization sorts molecules by shape as well as by size and class.[37] This distinguishing feature allows this separation technique to be applied to those systems which are difficult and often impossible to separate by well-known methods.

The reformate shown in Table VI, page 40, is also listed in Table VII, Appendix III, where two different inductors were individually applied. Carbon tetrachloride is shown in one extractive stage and 1,2,4-trichlorobenzene in three successive stages. Carbon tetrachloride obviously prefers cumene, n-propylbenzene and indan. The inductor 1,2,4-trichlorobenzene shows an extreme preference for pseudocumene, where the reformate composition is approximately thirty-four percent. In one state this feed composition is increased to almost seventy-two percent and in the third stage to about ninety-six percent.

Ternary mixtures are shown in Table VIII, Appendix VIII using these same two inductors. Carbon tetrachloride continues to show preference for n-propylbenzene. Considering the inductor 1,2,4-trichlorobenzene and comparing the two ternary systems of n-propylbenzene, m-ethyltoluene, p-ethyltoluene (System I) with m-ethyltoluene, p-ethyltoluene, o-ethyltoluene (System II), it is apparent that the presence of o-ethyltoluene in System II inhibits the selectivity of p-ethyltoluene. In System I the composition of p-ethyltoluene is increased by approximately one hundred two percent and in System II, where o-ethyltoluene is present, the composition of p-ethyltoluene is increased only twenty-seven percent.

The significance of this comparison is evident when considering Table VI, page 40. The boiling point of o-ethyltolune is significantly higher than both m-ethyltoluene and p-ethyltoluene whose boiling points are close together. O-ethyltoluene can be separated from the other two isomers by distillation and subsequently induced extractive crystallization can be applied to separate m-ethyltoluene and p-ethyltoluene.

A comparison of induced extractive crystallization with distillation is shown in Table IX, Appendix VIII. Xi is defined as the extent of separation and is a normalized number where 0 corresponds to no separation and 1 implies one hundred percent separation. Extent of separation, ξ, is defined in such a way that it can be

generally applied to any separation process and meaningful comparisons can be obtained for different processes.[35]

The comparison of extent of separation in Table VIII is one extractive stage for adduction versus one theoretical stage in distillation. Using the inductor, 1,2,4-trichlorobenzene, adduction is twenty-four times more effective than distillation for the system of m-ethyltoluene and p-ethyltoluene.

The binary systems in Table I, page 6, are mostly isomers of trimethylbenzene. An inductor yielding a high extent of separation is shown for several systems.

APPENDIX III-- METHODS OF CRYSTAL GROWTH

Methods employed for crystal growth are discussed in this appendix.

Initially, a crystal selected from the adducts formed in the procedure described by McCandless[8,55] was not suitable for a data collection. This method is described on page 14.

All real crystals contain defects. Some defects are inherent and cannot be avoided, others may be controlled within limits by thermal and mechanical treatments. In general, rapid growth of a crystal may introduce imperfections and twinning. The imperfections will create interference of diffraction patterns and decrease the number of reflections as well as increase the background noise in a data collection. Twinning introduces other serious problems for solution of a structure. These problems can be minimized if the environment is controlled to effect slow crystal growth.

The following illustrations describe alternate methods of crystal growth and the final resolution employed.

1) Three test tubes were filled with ten ml of thiourea dissolved in methanol. A pipette containing a mixture of aromatic and inductor was inserted into each test tube and two ml of the aromatic-inductor liquid was gently released at the bottom of the tube. A period of two weeks was

allowed to pass and a large crystal was formed at the interface of each test tube. This crystal was bulky and crude and quite insufficient for collecting diffraction data.

2) Both the thiourea-methanol solution and the aromatic-inductor mixture were placed in a closed container which prevented liquid-liquid contact, but allowed the vapors to share the same atmosphere. One month was allowed for diffusional growth and very fine crystals were detected. This method was abandoned due to the time factor; it was apparent that several more months of growth were required to produce larger crystals.

3) Efforts on selecting a suitable crystal from those adducts formed in the procedure described by McCandless[1,8] were continually under way. Patience and the gain of visual knowledge finally resulted in a wise choice of crystals. A polarizing microscope aided in establishing the visual requirements. This microscope was available through the Department of Chemistry at Montana State University.

In retrospect, a crystal obtained in any manner other than the final method employed would not have been scientifically sound. The method of growth can influence the relative proportions of the compounds present[2] and hence the degree of selectivity.

Therefore, the analysis must be performed on a crystal coming from the environment which corresponds to the adduct in which the analysis is related.

APPENDIX IV--CALCULATION FOR UNIT CELL COMPOSITION

Appendix IV contains a description of the method applied for obtaining the distribution of compounds in a unit cell.

The table shown below was constructed based on the weight percent composition supplied by Galbraith Laboratories for the adduct containing 1,2,3-trichlorobenzene and 1,2,4-trimethylbenzene.

atom	wt. %	mol. wt.	# mols	# mols ÷ .348
C	33.9	12.011	2.82	8.10
H	5.79	1.0079	5.74	16.49
N	22.48	14.007	1.605	4.6
Cl	12.35	35.453	0.348	1.0
S	25.0	32.06	0.78	2.24
O	0.48	15.999	0.030	0.0

The presence of oxygen was insignificant and, therefore, excluded in the formula determined from this table. The empirical formula is $C_{32}H_{66}N_{18}S_9Cl_4$.

Density is defined to be weight per unit volume.

$$D=\frac{wt}{V} = \frac{(\text{formula wt})(n)/6.023\times10^{23}}{(abc)(\sin\beta)(10^{-24})}$$

D = density
wt = weight
V = volume
n = # mols

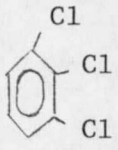
a,b,c = unit cell edge lengths in angstroms

β = angle between edge lengths a and c

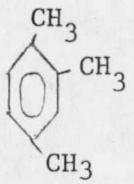
From Weissenburg photograph studies a = 12.644 Å, b = 15.328 Å, c = 9.828 Å and β = 113.85°. The measured density was approximately 1.27 g/ml. Substituting into the density equation,

$$(\text{formula wt})(n) = 1230 \text{ g} \qquad (1)$$

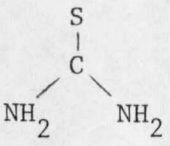
The compounds present in the adduct are shown schematically.



1,2,3-trichlorobenzene



1,2,4-trimethylbenzene



Thiourea

With the knowledge of these molecules, together with the empirical formula and symmetry evaluations, the formula per unit cell was roughly determined as $C_{33}H_{66}N_{24}S_{12}Cl_6$. Based on this formula, each unit cell contains approximately twelve thioureas, two 1,2,3-trichlorobenzenes and one 1,2,4-trimethylbenzene.

APPENDIX V--VAX/VMS COMPUTER PROGRAM LISTING

Appendix V contains a listing of the basic programs applied during the structure study of the adduct composed of 1,2,3-trichlorobenzene, 1,2,4-trimethylbenzene and thiourea.

Multan 78 contains the system of programs shown below.

NORMAL — This program takes the standard binary data file produced from data reduction and computes normalized structure amplitudes from the observed structure factors.

MULTAN — MULTAN consists of three logical sections:

1. SIGMA2
2. CONVERGE
3. FASTAN

CONVERGE locates starting reflections and assigns phase values to reflections which define the origin and enantiomorph. Other reflections are chosen which may also act as starting points. FASTAN determines phases for all reflections from each starting set produced by CONVERGE.

EXFFT — An E-Map is computed from a set of normalized structure factors.

SEARCH — Search locates the coordinates of the highest peaks in the E-Map. For a given molecular structure, it searches for groups of peaks which could form a molecule or a molecular fragment consisting of at least five atoms. The program also computes bond lengths and angles for each molecular fragment.

Each program successively updates the binary data file which becomes the feed for the following program.

The programs in X-Ray 76 are listed in alphabetical order.[50]

GENERL — General description of the -XRAY- system, its terms and use

ABSORB — Absorption correction

ABSORB — Diffractometer absorption correction

APHASE — Search of sigma-2 relationships for a set of possible phases

BONDAT — Generation of the coordinates of bonded atoms

BONDLA — Determination of contact and bond distances and angles with estimated errors

BUILDM — Find a connected set of atomic coordinates from input search of Fourier peaks

CELRDN — Cell reduction program

CONTRS — Draw Fourier maps on a line plotter

CRYLSQ	General crystallographic least squares program
CRYSET	Generate general equivalent positions from space group symbol
DATCO5	Treatment of initial diffractometer intensity data
DATRDN	Preparation of binary data file and preliminary treatment of data and symmetry
DELSIG	Display delta F as a function of FO or sin (theta)
DRAW	Fourier contouring program
DUMCOP	Dump or copy the binary data file
EC	Calculate normalized structure factors, E, and form translation function coefficients
EGEN	Estimation of normalized structure factors, and overall temperature and scale factors
FC	Structure factor calculation
FOUREF	Automatic block Fourier refinement of atomic parameters
FOURR	Fourier transformations to give Patterson, vector, electron density, difference, or E-Maps
LATCON	Least squares refinement of lattice parameters
LISTFC	Lists structure factors for publication
LOADAT	Load atomic parameters into the binary data file
LSQPL	Calculation of equations of 3-dimensional planes and lines

MODIFY	Binary data file editing and generation of pseudo data
MULDMP	Dump -XRAY- binary data file to give input for non-system -MULTAN-
MULTAN	XRAY adaption of Woolfson-Main-Germain multiple solution program
NORMSF	Preliminary data scaling, calculation of normalized structure factors and estimation of temperature factors
ORTEP	XRAY adaptation of Oak Ridge plotting program
PARAM	Least squares refinement of cell parameters from two theta data
PEKPIK	Search Fourier maps for peaks
PHASE	Search of sigma2 relationships for a set of possible phases (centric case)
PLOT	Produce plots for -ORTEP-, -PROJCT-, -CONTRS-, and connect to shop plotter or simulate plotter on line printer.
POWGEN	Powder patterns from single crystal data
PROJCT	Produce a plot of the projection of a molecule on a plane
REVIEW	Evaluation of direct phase determination
RIGBOD	Generation of rigid groups for use in least squares refinement

RLIST	Lists R values for various zones and other reflection classes
SINGEN	Forms triples for phase determination
STEPRF	Step refinement of atomic parameters at low resolution
TANGEN	Use of tangent formula to calculate phases
THEMA	Thermal motion analysis
WRITEU	Generation of write-up
WTANAL	Analysis of least squares weighting schemes
WRLSSQ	Calculation of least squares weighting schemes

The following program is not a part of the X-Ray 76 system, but uses the binary data file from DATRDN in X-Ray 76 as input.

EVAL	Calculates quasi-normalized structure factors based on a random-atom structure, and normalized structure factors based on known structural information, such as heavy atom sites, molecular configuration, oriented molecular-fragments and positioned molecular-fragments.
SINVAR	SINVAR generates triplet, quartet and quintet structure invariants.
GENTAN	GENTAN estimates structure factor phases using the invariants generated by SINVAR.
PREMAP	This program extracts a GENTAN-generated phase set from the binary data file, updates this file and outputs a binary data file suitable for FOURR.

PHISIN

PHISIN reviews phase sets and invariants generated by GENTAN and SINVAR. It is designed to provide information on the reliability of the invariants (by applying known phases) or for comparing different phase sets (generated by GENTAN).

APPENDIX VI--BASIC CONCEPTS OF CRYSTALLOGRAPHIC STRUCTURE ANALYSES

The content in Appendix VI includes a very rough outline of the factors involved in a crystallographic structure study.

General Description

An ideal crystalline substance is a homogeneous solid in which the atomic or molecular arrangement repeats by translation in three dimensions; the repeat distance and direction can be described by a three dimensional coordinate system. Internally, a crystal is composed of atoms oscillating about regular positions on a lattice,[45] repeating in accordance with the crystal system and symmetry. Externally, the crystal consists of a regular three-dimensional figure possessing certain symmetry characteristics. The formal classification of crystals and some common nomenclatures are specified in Appendix I.

A crystallographic structure study will ultimately establish all atomic positions and thermal vibration parameters. Bond distances and bond angles, as well as non-bonded contacts within the unit cell can be determined from the atomic positions. Raw data include information on unit cell parameters, crystal symmetry and diffraction intensities. The phases of the diffracted intensities are not directly observable, but are needed for solution of the structure.

The techniques of x-ray diffraction depend upon the fact that x-rays and electrons are scattered in characteristic and symmetrical ways by the regular arrays of atoms in the crystal.[45] The x-ray diffraction patterns are produced by the atoms at angles that are characteristic of the atomic arrangement, yielding a spectrum from which the atomic or molecular structures can be determined.

Requirements

The ability to completely solve for a given structure is contingent upon several major factors.

1. The proper selection of a suitable crystal. This can involve extensive trial-and-error procedures as well as attempts at duplicating known methods.*
2. The crystal must be stable. It must not deteriorate during usable time intervals and it must not break down under the x-ray beam. Various alternatives are available for stabilizing a given crystal.
3. Non-x-ray measurements can be helpful.
    a. elemental analysis
    b. molecular weight of unit cell
    c. crystal density
4. The actual data collection and the interpretation of this collection are the essence of a crystallographic

---

*Appendix III describes methods of crystal growth.

structure study. Two quite different methods can be employed.

a. photographic film methods

i. power camera
ii. Weissenburg camera
iii. oscillation camera
iv. precession camera

b. diffractometers

Data Collection

In general, the data collection (diffraction patterns) may be obtained from a single crystal. This crystal must be mounted such that lattice planes will successively come into reflecting positions when irradiated with a continuous x-ray beam. The intensities of each reflecting plane are recorded for that particular position. The phase angles for every reflection must be determined and are required to reconstruct atomic positions. Intensity measurements are collected for this purpose. The electron density distribution in the crystal cell is deduced from these intensities and phases. Ideally, the integrated intensity is a measure of the total number of photons of the characteristic wavelengths which are diffracted in a given direction by the crystal.[33]

The usual method of recording intensities for the diffracted x-rays is on a photographic film or some form of radiation counter. Generally, the photographic film methods are used for preliminary

crystal studies which help to establish the geometrical parameters and symmetry. Qualitatively, the same information is obtained from each of these cameras. However, the most favorable results are obtained by utilizing more than one method synchronously. Besides determining the unit cell parameters from the photographs, various methods are available for interpreting the relative intensities from the spots on the film.

Mechanical devices which use some form of radiation counter to measure the energy of diffracted beams, rather than taking a photographic record, are called diffractometers.[47] There are several different types of counters which can be incorporated into a diffraction instrument. They have different geometrical arrangements as do the various photographic film methods.

The most advanced diffractometers are completely computer automated. The use of a diffractometer of this quality would require very few, if any, preliminary studies, although any information available may be helpful.

Structure Solution

The actual solution for a given crystal structure can be realized in more than one fashion. Some of the procedures are the Patterson Function which is the Fourier transform of the intensities, various so called "direct methods," vector methods and trial-and-

error methods. Often the utilization of more than one method is imperative to obtain a complete structure determination.

Crystal structure determinations require the aid of a high speed computer. Most of the common operations have been programed for all the ordinary varieties of computers.[33]

As stated previously, the initial data collection constitutes the raw information from which crystal structures are derived. The raw intensity data requires various modifications to produce the basic structure factors used in a final structure determination and refinement.

Once a satisfactory phasing model is obtained, the application of several Fourier syntheses and least squares refinements will produce a final accurate model. An indication of how correct this model is likely to be can be obtained by comparing the observed structure factors with the calculated structure factors.

Limitations

A complete solution for a given crystalline structure is never guaranteed, although with access to the most modern equipment and computer system, the probability is quite high. Since the methods applied for phase determination are based on statistical analyses, a large collection of diffracted intensities are needed. Problems may arise if the internal arrangement of atoms is either partially

or completely disordered, and a rapid decline of intensities in the data collection will indicate that these problems do exist.

The field of crystallography has progressed rapidly in recent years. Computer technology is largely responsible for these advancements. The quality of the diffraction equipment and the computer facilities directly influence the net outcome and the time factor required for a particular structure study.

APPENDIX VII--STRUCTURAL REPORT BY MOLECULAR STRUCTURE CORPORATION

All of the information in Appendix VII was taken directly from the structural report provided by Molecular Structure Corporation. The structure determination for the adduct containing 1,2,4-trimethylbenzene (referred to in this report as 1,2,5-trichlorobenzene) was performed by the staff of Molecular Structure Corporation: Dr. M. W. Extine, Ms. R. A. Meisner, and Dr. J. M. Troup. Data and diagrams which pertain to this structural study are located in Appendix VIII. This information is included in Tables X, XI, XII, XIII, and XIV and Figures II and III. Table V, page 29, also contains data resulting from the structural study.

Data Collection

A colorless needlelike crystal of the 6:1 thiourea + 1,2,5-trimethylbenzene adduct (C15 H36 N12 S6) having approximate dimensions of Ø.15 x Ø.15 x Ø.35 mm was mounted in a glass capillary with its long axis roughly parallel to the phi axis of the goniometer. Preliminary examination and data collection were performed with Cu Kα radiation (λ = 1.54184 A) on an Enraf-Nonius CAD4 computer controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochromator.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles

of 24 reflections in the range 11 < θ < 27°, measured by the computer controlled diagonal slit method of centering. The monoclinic cell parameters and calculated volume are: a = 12.337(2), b = 15.126(2), c = 1Ø,ØØ3(2) A, β = 112.74(1) V = 1721.5A^3. For Z = 2 and F.W. = 576.92 the calculated density is 1.11 g/cm^3. As a check on crystal quality, omega scans of several intense reflections were measured; the width at half-height was Ø.3Ø° with a take-off angle of 2.8°, indicating good crystal quality. From the systematic absences of:

$$ØkØ \quad k=2n+1$$

$$hØ1 \quad l=2n+1$$

and from subsequent least-squares refinement, the space group was determined to be P2-1/c (# 14).

The data were collected at a temperature of 23 ± 1° using the w-θ scan technique. The scan rate varied from 2 to 2Ø°/min (in omega). The variable scan rate allows rapid data collection for intense reflections where a fast scan rate is used and assures good counting statistics for weak reflections where a slow scan rate is used. Data were collected to a maximum 2θ of 12Ø.Ø°. The scan range (in deg.) was determined as a function of θ to correct for the separation of the Kα doublet;[49] the scan width was calculated as follows:

$$\theta \text{ scan width} = Ø.6 + Ø.3ØØ \tan \theta$$

Moving-crystal moving-counter background counts were made by scanning an additional 25% above and below this range. Thus the ratio of peak

counting time to background counting time was 2:1. The counter aperture was also adjusted as a function of θ. The horizontal aperture width ranged from 2.Ø to 3.7 mm; the vertical aperture was set at 2.Ø mm. The diameter of the incident beam collimator was 0.7 mm and the crystal to detector distance was 21 cm. For intense reflections an attenuator was automatically inserted in front of the detector; the attenuator factor was 15.5.

Data Reduction

A total of 2743 reflections were collected, of which 2546 were unique and not systematically absent. As a check on crystal and electronic stability, three representative reflections were measured every 41 minutes. The intensities of these standards remained constant within experimental error throughout data collection. No decay correction was applied.

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 37.1 cm^{-1} for Cu Kα radiation. No absorption correction was made. An extinction correction was not necessary.

Structure Solution and Refinement

The structure was solved by direct methods. Using 175 reflections (minimum E of 2.ØØ) and 2247 relationships, a total of 16 phase sets were produced. The three sulfur atoms were located from an E-map prepared from the phase set with probability statistics: absolute figure of merit = 1.26, residual = Ø.14, and psi zero = 2.Ø1Ø.

The remaining atoms were located in succeeding difference Fourier syntheses. The trimethylbenzene molecules are disordered, both translationally and through the inversion centers. The atoms labeled C4 through C13 were refined at half occupancy. To fit the proposed disorder scheme, atoms C5 and C1Ø should have been refined at Ø.25 occupancy. However, this value gave somewhat low isotropic temperature factors for these atoms. Further analysis of the disorder scheme was hindered by the relatively low resolution of the data. The thiourea atoms were refined anisotropically, the disordered carbon atoms of the trimethylbenzene molecules were refined isotropically. Hydrogen atoms were not included in the calculations. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma w(Fo - Fc)^2$ and the weight w is defined as $4Fo^2/\sigma^2(Fo^2)$.

The standard deviation on intensities, $\sigma(Fo^2)$, is defined as follows:

$$\sigma^2(Fo^2) = [S^2 (C + R^2B) + (pFo^2)^2] / Lp^2$$

where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count, Lp is the Lorentz-polarization factor, and the parameter p is a factor introduced to downweight intense reflections. Here p was set to Ø.Ø6Ø.

Scattering factors were taken from Cromer and Waber.[32] Anomalous dispersion effects were included in Fc;[50] the values for

$\Delta f'$ and $\Delta f''$ were those of Cromer.[32] Only the 771 reflections having intensities greater than 3.Ø times their standard deviation were used in the refinements. The final cycle of refinement included 149 variable parameters and converged with unweighted and weighted agreement factors of:

$$R1 = \Sigma \quad Fo - Fc \quad / \Sigma \quad Fo = Ø.Ø75$$

$$R2 = SQRT \left(\Sigma w \left(Fo - Fc \right)^2 / \Sigma w Fo^2 \right) = Ø.114$$

The standard deviation of an observation of unit weight was 2.57. The highest peak in the final difference Fourier had a height of $Ø.5Ø$ e/A^2 with an estimated error based on ΔF[51] of $Ø.1Ø$. Plots of $\Sigma w(Fo - Fc)^2$ versus Fo, reflection order in data collection, sin θ/λ, and various classes of indices showed no unusual trends.

All calculations were performed on linked PDP-11/45-11/6Ø computers using the Enraf-Nonius Structure Determination Package as well as private programs of Molecular Structure Corporation.

APPENDIX VIII--TABLES AND FIGURES FOR APPENDIX III AND APPENDIX VII

The tables and figures which are contained in Appendix VIII are referred to in Appendix III as well as Appendix VII.

TABLE VII

SEPARATION OF THE C_9 ALKYLBENZENES USING CCl_4
AND 1,2,4 TRICHLOROBENZENE AS INDUCTORS
COMPOSITION IN WT. %

Inductor	CCl_4			1,2,4 Trichlorobenzene			
Component	Feed	Residue	Adduct	Residue #1	Adduct #1	Adduct #2	Adduct #3
cumene	0.9	0.5	3.9	1.1	0	0	0
n-propylbenzene	5.6	4.5	24.4	8.5	0.3	0	0
m-ethyltoluene	21.5	22.2	8.5	30.7	5.0	0.3	0
p-ethyltoluene	9.7	9.6	10.9	12.2	4.9	0.9	trace
mesitylene	10.0	10.7	0.1	16.0	0	0	0
o-ethyltoluene	10.1	9.7	15.2	12.2	5.3	1.2	trace
pseudocumene	34.0	35.3	21.2	13.9	71.7	87.7	95.9
hemimellitene	6.4	6.7	1.9	3.7	11.1	9.9	4.1
indan	1.8	0.9	14.0	1.6	1.7	0	0

TABLE VIII

SEPARATION OF TERNARY MIXTURES OF SOME OF THE C_9 ALKYLBENZENES
COMPOSITION IN WT. %

Inductor		CCl_4		1,2,4 TCB	
Component	Feed	Residue	Adduct	Residue	Adduct
n-propylbenzene	0.162	0.149	0.519	0.158	0.047
m-ethyltoluene	0.606	0.619	0.235	0.637	0.485
p-ethyltoluene	0.232	0.232	0.246	0.205	0.468
mesitylene	0.349	0.356	0.197	0.502	0.011
pseudocumene	0.356	0.353	0.458	0.241	0.620
hemimellitene	0.295	0.291	0.345	0.257	0.369
m-ethyltoluene	0.353	0.365	0.202	0.399	0.183
p-ethyltoluene	0.315	0.310	0.342	0.294	0.399
o-ethyltoluene	0.332	0.325	0.456	0.306	0.418

TABLE IX

COMPARISON OF EXTRACTIVE CRYSTALLIZATION WITH DISTILLATION

System	Inductor	α Adduct	ξ Adduct.	α Distillation*	ξ max Distillation	ξ Adduct / ξ Dist.
mesitylene/o-ethyltoluene	1,2,4 TCB	45.0	.09-.26	1.01	0.002	45-130
mesitylene/o-ethyltoluene	CCl_4	3.81	.03-.10	1.01	0.002	15-50
hemimellilene/indan	1,2,4 TCB	2.32	.23-.34	1.06	.015	15-22
hemimellilene/indan	CCl_4	9.80	.13-.34	1.06	.015	9-22
p-ethyltoluene/m-ethyltoluene	1,2,4 TCB	3.29	.13-.23	1.02	.005	26-46
p-ethyltoluene/m-ethyltoluene	CCl_4	2.45	.03-.08	1.02	.005	6-16
pseudocumene/hemimellitene	1,2,4 TCB	1.96	.13-.23	1.24	.054	2-4
pseudocumene/hemimellitene	1,2,3 TCB	3.80	.31	1.24	.054	6
hemimellitene/mesitylene	1,2,4 TCB	165.4	.56	1.42	.087	6
pseudocumene/mesitylene	1,2,4 TCB	708.0	.64	1.14	.033	19
o-ethyltoluene/m-ethyltoluene	1,2,4 TCB	3.10	.17	1.10	.024	7
o-ethyltoluene/m-ethyltoluene	CCl_4	3.00	.07	1.10	.024	3
o-ethyltoluene/p-ethyltoluene	1,2,4 TCB	1.03	.004	1.08	.019	.2
o-ethyltoluene/p-ethyltoluene	CCl_4	1.40	.06	1.08	.019	3
m-ethyltoluene/p-ethyltoluene	1,2,4 TCB	2.90	.12	1.02	.005	24
m-ethyltoluene/p-ethyltoluene	CCl_4	2.90	.07	1.02	.005	14

* Assuming Raoults Law and using Vapor pressure data from Weast (1977)

TABLE X

CRYSTAL DATA

6:1 thiourea + 1,2,5-trimethylbenzene adduct

C15 H36 N12 S6

F.W. 576.92 F(ØØØ) = 612

Crystal dimensions: Ø.15 x Ø.15 x Ø.35 mm

Peak width at half-height = Ø.2Ø°

Cu Kα radiation (λ = 1.5418Ø A)

Temperature = 23 ± 1°

Monoclinic space group P2-1/c

a = 12.337 (2) A b = 15.126 (2) A c = 1Ø.ØØ3 (2) A

β = 112.74 (1)

V = 1721.5 A^2

Z = 2 ρ = 1.11 g/cm^2

μ = 37.1 cm-1

TABLE XI

INTENSITY MEASUREMENTS

Instrument:	Enraf-Nonius CAD4 diffractometer
Monochromator:	Graphite crystal, incident beam
Attenuator:	Ni foil, factor 15.5
Take-off angle:	2.8°
Detector aperture:	2.Ø to 3.7 mm horizontal
	2.Ø mm vertical
Crystal-detector dist.:	21 cm
Scan type:	w-θ
Scan rate:	2 - 2Ø°/min (in omega)
Scan width, deg:	Ø.6 + Ø.3ØØ tan θ
Maximum 2θ:	12Ø.Ø°
No. of refl. measured:	2743 total, 2546 unique
Corrections:	Lorentz-polarization

TABLE XII

STRUCTURE SOLUTION AND REFINEMENT

Solution:	Direct methods
Hydrogen atoms:	Not included
Refinement:	Full-matrix least-squares
Minimization function:	$\Sigma w(\|Fo\|-\|Fc\|)^2$
Least-squares weights:	$4Fo^2/\sigma^2(Fo^2)$
"Ignorance" factor:	Ø.Ø6Ø
Anomalous dispersion:	All non-hydrogen atoms
Reflections included:	771 with $Fo^2>3.Ø\sigma(Fo^2)$
Parameters refined:	149
Unweighted agreement factor:	Ø.Ø75
Weighted agreement factor:	Ø.114
Factor including unobs. data:	Ø.294
Esd of obs. of unit weight:	2.57
Convergence, largest shift:	Ø.Ø8σ
High peak in final diff. map:	Ø.5Ø (9) e/A^2
Computer hardware:	Linked PDP-11/45-11/6Ø
Computer software:	Enraf-Nonius SDP and private programs of Molecular Structure Corporation

TABLE XIII

BOND DISTANCES IN ANGSTROMS

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
S1	C1	1.736(12)	C3	N6	1.345(13)	C7	C12	1.53(4)
C1	N1	1.317(13)	C4	C5	1.52(4)	C8	C9	1.32(3)
C1	N2	1.33Ø(13)	C4	C5	1.29(4)	C9	C1Ø	1.91(4)
S2	C2	1.737(12)	C4	C13	1.24(3)	C9	C1Ø	1.44(3)
C2	N3	1.33Ø(13)	C5	C5	1.35(6)	C1Ø	C11	1.28(3)
C2	N4	1.36Ø(13)	C5	C6	1.35(4)	C11	C12	1.28(3)
S3	C3	1.75Ø(12)	C6	C7	1.45(4)	C12	C13	1.45(4)
C3	N5	1.333(13)	C7	C8	1.33(4)			

Numbers in parenteses are estimated standard deviations in the least significant digits.

TABLE XIV

BOND ANGLES IN DEGREES

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
S1	C1	N1	12Ø.(1)	C4	C5	C4	124.(3)	C8	C9	C1Ø	156.(4)
S2	C1	N2	119.(1)	C4	C5	C5	53.(2)	C1Ø	C9	C1Ø	75.(3)
N1	C1	N2	121.(1)	C4	C5	C6	1ØØ.(4)	C9	C1Ø	C9	1Ø5.(3)
S2	C2	N3	121.(1)	C4	C5	C5	7Ø.(3)	C9	C1Ø	C11	9Ø.(3)
S2	C2	N4	118.(1)	C4	C5	C6	136.(4)	C9	C1Ø	C11	166.(4)
N3	C2	N4	12Ø.(1)	C5	C5	C6	153.(5)	C1Ø	C11	C12	146.(3)
S3	C3	N5	119.(1)	C5	C6	C7	136.(4)	C7	C12	C11	122.(3)
S3	C3	N6	118.(1)	C6	C7	C8	127.(4)	C7	C12	C13	98.(3)
N5	C3	N6	123.(1)	C6	C7	C12	121.(3)	C11	C12	C13	14Ø.(4)
C5	C4	C5	56.(3)	C8	C7	C12	112.(3)	C4	C13	C12	14Ø.(4)
C5	C4	C13	125.(4)	C7	C8	C9	121.(3)				
C5	C4	C13	178.(3)	C8	C9	C1Ø	128.(3)				

Numbers in parentheses are estimated standard deviations in the least significant digits.

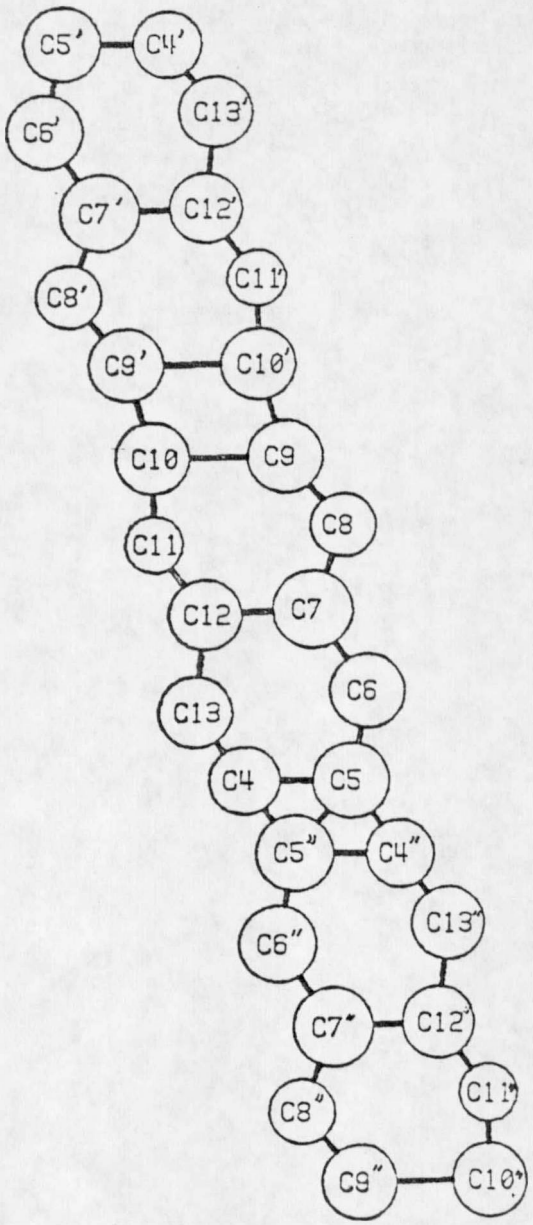


FIGURE II. SINGLE MOLECULE SHOWING 50% PROBABILITY ELLIPSOIDS.

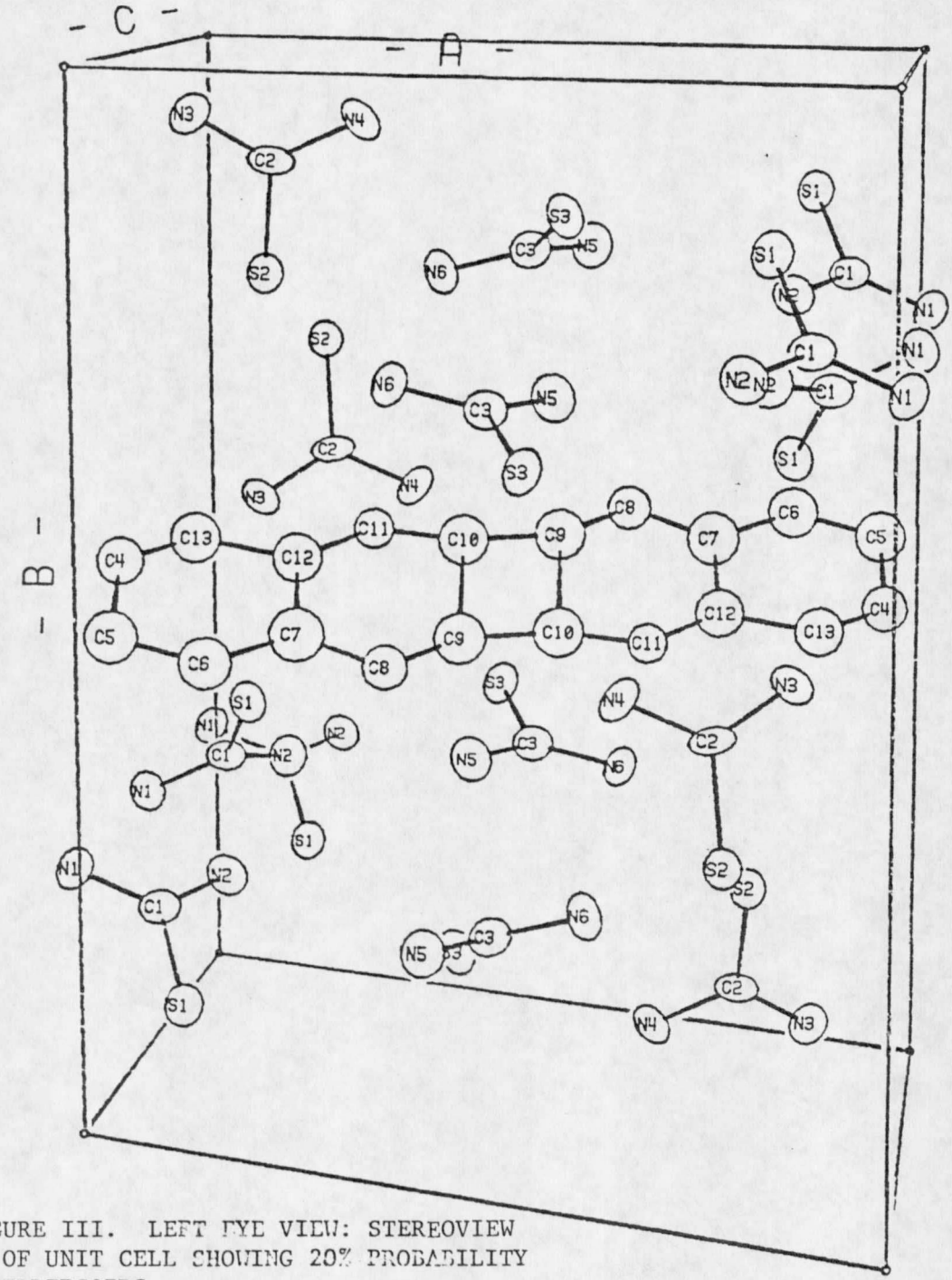


FIGURE III. LEFT EYE VIEW: STEREOVIEW OF UNIT CELL SHOWING 20% PROBABILITY ELLIPSOIDS.

MONTANA STATE UNIVERSITY LIBRARIES
stks N378.W459@Theses
Separate aromatic compounds by forming a
RL
3 1762 00113128 1

N378
W459
cop.2
Welling, R. I.
Separate aromatic compounds by forming adducts with Thiourea

DATE	ISSUED TO

MAIN
N378
W459
cop. 2
GAYL