



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
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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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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

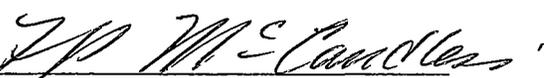
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ABSTRACT

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 hydrocarbons²⁷ 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

*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

* 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)

<u>System</u>	<u>Inductor</u>	<u>Selectivity</u>	<u>α</u>	<u>ξ</u>
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 Radzitzky¹⁸ provided a good discussion of laboratory investigations wherein urea was used as a dewaxing agent.

An article by Fetterly⁴¹ 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 Redlich⁵ and in his report he included composition and equilibrium constants for several adducts as well as approximate activity values for these adducts.

Lenne⁵⁶ 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 $R\bar{3}2/c-D_{3d}^6$.

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.

McLaughlin³⁷ 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.

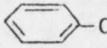
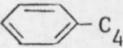
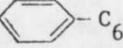
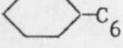
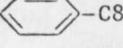
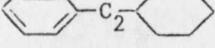
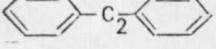
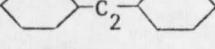
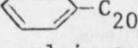
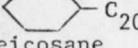
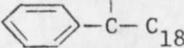
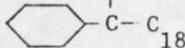
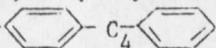
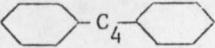
The information and ideas proposed in this thesis report have shown that the discrepancies reported in the literature concerning the structure of adducts with thiourea need not be a disagreement, but may represent true findings; crystal structures of adducts formed with thiourea can vary.

McLaughlin³⁷ 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 Radzitzky³ 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

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

*Reproduced from McLaughlin³⁷

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

<u>Adducts Containing</u>	<u>Density (g/ml)</u>	<u>Melting Point</u>	<u>Space Group</u>	<u>Empirical Formula</u>
1,2,3,-tri- chlorobenzene 1,2,4-tri- methylbenzene	1.27	178 C	P2 ₁ /c	C ₃₂ H ₆₆ N ₁₈ S ₉ Cl ₄
1,2,4-tri- chlorobenzene 1,2,3,-tri- methylbenzene	1.3		P2 ₁ /c	C ₈ H ₁₆ N ₆ S ₃ Cl ₂
1,2,4-tri- chlorobenzene 1,2,4,-tri- methylbenzene	1.3	178 C	P2 ₁ /c	C ₆ H ₁₂ N ₄ S ₂ Cl

TABLE IV
COMPOUNDS TESTED FOR ADDUCTABILITY

<u>COMPOUND</u>	<u>ADDUCTABILITY</u>
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.

Diffractionmeter

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 Diffractionmeter equipped with a scintillation counter, pulse-height discriminator, and G.E. single crystal orienter was employed. A 0-20 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.

