Aromatic Compounds

When a new compound, C₆H₆, was discovered in ~1830 no one could imagine a structure. Many were proposed, and a generation of debate followed. In 1858 carbon chains were proposed, in 1860, August Kekule had the revolutionary insight—aring Kekule's structure was considered quite bizarre.

Since benzene forms only 1,2-dichloro product, Kekule proposed this fast interconversion:

\[
\begin{array}{c}
\text{Cl} \\
\text{C} \\
\text{C}
\end{array} \rightleftharpoons \begin{array}{c}
\text{Cl} \\
\text{C} \\
\text{C}
\end{array}
\]

Which is the forerunner of our current resonance structure:

\[
\begin{array}{c}
\text{C} \\
\text{C}
\end{array} \rightleftharpoons \begin{array}{c}
\text{C} \\
\text{C}
\end{array}
\]

Kekule's structures

These are only convenient constructs, a better picture is:

\[0\]

We find by hydrogenation that benzene has 36 kcal/mol resonance stabilization.

This stability means that benzene does not undergo alkene reaction:

\[
\text{C}=\text{C} + \text{B}_2Cl_2 \xrightarrow{\text{CCl}_4} -\text{C}=-\text{C}^- + \text{B}_2 + \text{B}_2
\]

The molecular orbitals of benzene:

\[\text{This is the lowest of 6 MOs} \]

\[\text{All bonding}\]

The energy diagram of benzene MOs:

\[\text{All 6 } \pi \text{-e-} \]

\[\text{Isolated orbital MOs} \]

\[\text{Very stable}\]
In contrast to benzene, the \( 4 \pi \) of cyclobutadiene occupy less favorable mo.

\[ \pi^+ \quad \pi^2 \quad \pi^3 \quad \pi^4 \]

The compound has 2 unpaired electrons in orbitals of bond order zero.

So, you can draw 2 resonance structures for cyclobutadiene:

\[ \square \leftrightarrow \square \]

But the MO picture says no resonance stabilization.

Aromatic, antiaromatic, nonaromatic

We compare many cyclic, conjugated systems to be aromatic:

1) Cyclic, with conjugated \( \pi \) bonds
2) Each ring atom must have a \( \sigma \) orbital
3) These \( \sigma \) orbitals must overlap continuously (usually planar)
4) Delocalization of the \( \pi \) electrons must result in lower energy.

An antiaromatic compound meets criteria 1-3 but \( \pi \) delocalization increases energy \( \square \) less stable than \( \square \) open chain.

Violating criteria 1-3 means \( \square \) nonaromatic.

\( \square \rightarrow \square \) similar stability \( \square \) \( \square \) \( \text{CH}_3 \) \( \text{CH}_3 \).

To criteria 1-4 we add Hückel's rule:

Aromatic if \( \# \pi \) electrons \( \equiv 4N + 2 \) where \( N \) is an integer.

\[ N = 1 \rightarrow 6 \pi \text{ electrons} \]
\[ N = 0 \rightarrow 2 \pi \text{ electrons} \]
\[ N = 2 \rightarrow 10 \pi \text{ electrons} \]

Most large ring systems are nonplanar, therefore nonaromatic.

Some large \( 4N + 2 \) annulenes are aromatic.

\( [14] \)-annulene aromatic

Fused ring systems can be planar \( \square \) napththalene aromatic.
THE MO DERIVATION OF HÜCKELS RULE

MO's IN THESE SYSTEMS HAVE 1 LOWEST FILLED MO → THE "+2"
AND PAIRS OF HIGHER LEVEL MO's FILLED WITH 4 ELECTRONS → THE "4N+2"
IF THERE ARE ONLY 2 ELECTRONS FOR THESE 2 MO's THE
SHELL IS HALF FILLED, ANTIAROMATIC, LIKE CYCLOBUTADIENE

ROMATIC IONS

Cyclopentadiene

IT IS UNUSUALLY ACIDIC

\[ \text{H}^+ + \text{strong base} \rightarrow \text{C}_{2}^{\text{H}_{5}}^- + \text{BH} \]

4N+2 AROMATIC

THE CYCLOPENTA DiENE ION HAS
4 N ELECTRONS → ANTIAROMATIC

The

Cycloheptatrienyl

Enylic cation is also 4N+2 aromatic

IT THE ANION IS ANTIAROMATIC

'COHERENT CYCLOHEPT ATRIENYL

ENYLCATION IS ALSO 4 N+2 AROMATIC

IT THE ANION IS ANTIAROMATIC

COMMON NAME TROPYLIUM

ION

REPRESENTS THE MOST STABLE CARBOCATION WE'VE SEEN

VERY UNUSUAL DIANION OF CYCLOOCTA TETRAE NE CAN BE MADE

\[ \text{C}_{8} \rightarrow 2^{K^0} \rightarrow \text{C}_{8}^- \]

PLANEAR

4N+2 AROMATIC

NEXT PAGE SUMMARIZES AROMATIC, ANTIAROMATIC RULES

ETEROCYCLIC AROMATIC COMPOUNDS

HETEROCYCLIC COMPOUND S CONTAIN HETERATOMS N, S, O

PYRIDINE IS THE AROMATIC ANALOG OF BENZENE WITH N IN THE RING

IT IS BASIC, LIKE AMMONIA →

PYRIDINIUM ION

\[ \text{H} \]

ION
Two pi-electron systems (aromatic)

\[ \text{cyclopropenyl cation (cyclopropenium ion)} \]

Four pi-electron systems (antiaromatic)

- cyclobutadiene
- cyclopropenyl anion
- cyclopentadienyl cation

Six pi-electron systems (aromatic)

- benzene
- cyclopentadienyl anion (cyclopentadienide ion)
- cycloheptatrienyl cation (tropylium ion)
- pyridine
- pyrrole
- furan

Eight pi-electron systems (antiaromatic if planar)

- cyclooctatetraene (not planar)
- cycloheptatrienyl anion
- cyclononatetraenyl cation
- pentalene

Ten pi-electron systems (aromatic)

- naphthalene
- azulene
- cyclononatetraenyl anion
- cyclooctatetraenyl dianion
- indole

(Naphthalene can also be considered as two fused benzenes.)

Twelve pi-electron systems (antiaromatic if planar)

- [12]annulene (not planar)
- heptalene

The criteria for Hückel's rule require a ring of atoms, all with unhybridized \( p \) orbitals overlapping in a continuous ring. In discussing aromaticity, we have considered only compounds composed of rings of \( sp^2 \) hybrid carbon atoms. **Heterocyclic compounds**, with rings containing \( sp^2 \) hybridized atoms of other elements, can also be aromatic. Nitrogen, oxygen, and sulfur are the most common heteroatoms in heterocyclic aromatic compounds.
HETERO CYCLIC AROMATICS

PYRrole
FURAN
THIOPHENE

AN ISO ELECTRONIC SERIES WITH 6 IT ELECTRONS

OLYNUCLEAR AROMATIC HYDROCARBONS (PAH)
FUSED RING SYSTEMS

NAPHTHALENE
ANTHRACENE
PYRENE
BENZO[AL]PYRENE

THE HIGHER PAH ARE CARCINOGENIC
SUCH AS PYRENE AND B&AP
FOUND IN COMBUSTION PRODUCTS - FOREST FIRES, ENGINE EXHAUST, CIGARETTES

OMERCIATURE OF BENZENE DERIVATIVES
MANY COMMON NAMES

PHENOL
CARBOLIC ACID
TOLUENE
ANILINE
ANISOLE
STYRENE
BENZALDEHYDE
BENZOIC ACID

COMPOUNDS MAY BE NAMED AS DERIVATIVES OF BENZENE

ALKYL BENZENES

HYDROBENZENE
CHLOROBENZENE
NITROBENZENE

ENZENE AS A SUBSTITUENT IS CALLED PHENYL (MAY BE ABBREVIATED AS PH OR \( \phi \)) IN CONDENSED STRUCTURES

\( \phi_3 CH \)

ethylene ether
TRIPHENYL METHANE

SUBSTITUTED BENZENES ARE CALLED ORTHO (1,2), META (1,3), PARA (1,4)

THIOCHLOROBENZENE
DICHLOROBENZENE
METANITROTOLUENE
PARANITRO PHENOL
BENZENES WITH 3 OR MORE SUBSTITUENTS ARE NUMBERED 1 IS ASSIGNED TO THE CARBON BEARING THE FUNCTIONAL GROUP THAT DEFINES THE BASE NAME

2,4-DINITROPHENOL  3-DROMO-5-CHLORO BENZOIC ACID

SOME MORE COMMON NAMES

TOLUENE  O-TOLUIC ACID  M-TOLUIDINE  P-CRESOL  O-XYLENE

IE 7 CARBON UNIT IS CALLED BENZYL

BENZYL BROMIDE  BENZYL ALCOHOL

FINALLY, AROMATIC COMPOUNDS ARE SOMETIMES CALLED ARENES

AR- FOR SHORT  AR-OH  AR-NH₂
ARYL AS SUBSTITUENT  ARYLACETYLENE  ARYLAMINE

PHYSICAL PROPERTIES

HIGH SYMMETRY MEANS LOW POLARITY IN THIS SERIES

<table>
<thead>
<tr>
<th></th>
<th>MOCl₂</th>
<th>MOCB</th>
<th>POCB</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP</td>
<td>181°C</td>
<td>173°C</td>
<td>170°C</td>
</tr>
<tr>
<td>mp</td>
<td>-17°C</td>
<td>-25°C</td>
<td>54°C</td>
</tr>
</tbody>
</table>

HIGH SYMMETRY GIVES GOOD CRYSTAL PACKING

INFRARED SPECTROSCOPY OF AROMATIC COMPOUNDS

SR  C=C STRETCH 1600 LOWEST OF THE C=C STRETCHES

MASS  BENZYLIC COMPOUNDS CLEAVE TO STABLE BENZYLIC CATIONS

\[ \text{CH}_2^+ \quad \text{C}_7\text{H}_7 = 91 \]

MR  AR-H  6.5-8.2 ppm HIGHER SHIFTS FROM WITHDRAWING SUBSTITUENTS, \(-\text{CN}^-, -\text{C}^-, -\text{NO}_2\)

LOWER SHIFTS FROM DONATING \(-\text{OH}, -\text{OR}, -\text{NH}_2\)
LECTURE NOTES FOR ORGANIC CHEMISTRY © MM 2011

ELECTROPHILIC AROMATIC SUBSTITUTION

\[
\begin{align*}
\text{RING ELECTRONS} & \quad \text{ATTACK ELECTROPHILE} \\
\text{ABSTRACTION OF } H^+ & \quad \text{SUBSTITUTION PRODUCT} \\
\text{AROMATICITY IS LOST} & \quad \text{EXOTHERMIC}
\end{align*}
\]

\[
\text{THE SIGMA COMPLEX RESONANCE STABILIZED}
\]

\[
\text{HIGHLY ENDOThERMIC RATE DETERMINING}
\]

\[
\text{MANY DIFFERENT ELECTROPHILES CAN BE USED}
\]

\[
\text{SUMMARY PG 356}
\]

HALOGENATION

\[
\begin{align*}
\text{Br}_2 & \quad \text{PG 326} \\
F_2\text{Br}_3 & \quad \text{FOR MECHANISM}
\end{align*}
\]

\[
\begin{align*}
\text{Cl}_2 & \quad \text{HCl} \\
\text{I}_2 & \quad \text{HNO}_3
\end{align*}
\]

ITRATION

\[
\begin{align*}
\text{HNO}_3 & \quad \text{H}_2\text{SO}_4
\end{align*}
\]

NITRATION

\[
\begin{align*}
\text{NO}_2 & \quad \text{HNO}_3 + \text{H}_2\text{SO}_4 \text{ PRODUCE THE NITRONIUM ION} \\
\text{H}\text{NO}_3 & \quad \text{d-O-N=O: WHICH IS THE ELECTROPHILE}
\end{align*}
\]

SULFONATION

\[
\begin{align*}
\text{SO}_3 & \quad \text{H}_2\text{SO}_4 \\
\text{H}_2\text{SO}_4, \text{HEAT} & \quad \text{SO}_3 \text{ IS THE ELECTROPHILE}
\end{align*}
\]

SULFONATION IS REVERSIBLE

\[
\text{SINCE DESULFONATION SUBSTITUTES A } H \text{ ON THE RING, IT PROVIDES}
\]

\[
\text{A SYNTHESIS OF } C_6\text{O}_6
\]

\[
\begin{align*}
\text{SO}_3 & \quad \text{LARGE EXCESS} \\
\text{D}_2\text{SO}_4/D_2O
\end{align*}
\]

ACTIONS OF SUBSTITUTED BENZENES

ACTIVATION, DEACTIVATION, DIRECTING GROUPS
NITRATION OF TOLUENE

TOLUENE REACTS 25X FASTER THAN BENZENE

TOLUENE IS "ACTIVATED" AND THE METHYL IS THE ACTIVATOR

ACTIVATED RINGS ARE SUBSTITUTED MOSTLY AT O, P, POSITIONS

\[
\begin{align*}
\text{CH}_3 & \quad \text{HNO}_3 \quad \text{H}_2\text{SO}_4 & \quad \text{CH}_3 & \quad \text{HNO}_3 \\
& & \text{CH}_3 \text{NO}_2 & & \text{CH}_3 \text{NO}_2 \\
\text{O-NITROTOLUENE} & 40\% & \text{M-NITROTOLUENE} & 3\% & \text{p-NITROTOLUENE} & 57\%
\end{align*}
\]

RANDOM NITRATION WOULD YIELD 40\% 40\% 20%.

THE STRUCTURE OF THE SIGMA COMPLEX REVEALS O, P SUBSTITUTION IS

STABILIZED BY A 3° CATION, WHILE META IS NOT

THE STABILIZING EFFECT OF ANY ELECTRON DONATING GROUP HAS THIS SAME

POSITIONAL PREFERENCE AND REACTION RATE ENHANCEMENT

TREMELY STRONG ACTIVATION COMES FROM SUBSTITUTENTS WITH

NO NONING ELECTRONS

TOLUENE REACTS 10,000 TIMES FASTER THAN BENZENE

\[
\begin{align*}
\text{OCH}_3 & \quad \text{HNO}_3 \quad \text{H}_2\text{SO}_4 & \quad \text{OCH}_3 & \quad \text{HNO}_3 \\
& & \text{OCH}_3 \text{NO}_2 & & \text{OCH}_3 \text{NO}_2 \\
\text{ANISOLE} & \text{ORTHODO} 45\% \text{PARA} 55\% \text{META} < 0
\end{align*}
\]

RESONANCE STRUCTURES OF THE SIGMA COMPLEX

ORTHODO ATTACK

\[
\begin{align*}
\text{NO}_2 & \quad \text{H}_2\text{O} & \quad \text{NO}_2 & \quad \text{H}_2\text{O} \\
\text{H} & & \text{H} &
\end{align*}
\]

EXTRA STABILIZATION

BUT THERE IS NO EXTRA STABILIZATION FOR META ATTACK

\[
\begin{align*}
\text{OCH}_3 & \quad \text{NO}_2 & \quad \text{OCH}_3 & \quad \text{NO}_2 \\
& & &
\end{align*}
\]

THE + CHARGE IS NEVER ON THE

RIGHT CARBON (THE -OCH$_3$ CARBON)

THE METHOXY GROUP IS SO STRONGLY ACTIVATING THAT NO Fe$_2$B$_3$ IS NEEDED

\[
\begin{align*}
\text{OCH}_3 & \quad \text{H}_2\text{O} & \quad \text{OCH}_3 & \quad \text{H}_2\text{O} \\
& & &
\end{align*}
\]

AMINO (-NH$_2$) GROUPS LIKEWISE ACTIVATE

SEE SUMMARY OF ACTIVATING, O, P DIRECTORS
Deactivating Substituents (Meta Directors)

Nitrobenzene reacts $10^5$ slower than benzene. O, P positions are most strongly deactivated, leaving meta positions most reactive (least deactivated).

In nitrobenzene, the nitrogen carries a formal charge.

\[
\text{INDUCTIVE EFFECT}
\]

Figure 17-4 shows the RCO for nitrobenzene reactions. O and P sigma complexes are highly destabilized in resonance forms where the + charge is on the carbon bearing the nitrogen.

Most deactivating groups are O, PMETA DIRECTORS

Any substituent with a formal + charge or partial + charge deactivates and META DIRECTS.

For example, the carbonyl group, $\text{CH}_2\text{O}$.

Ortho attack (and para) is destabilized.

Deactivating meta directors are summarized on pg 247, 680.

Nally, Halogens

The halogens are both inductively withdrawing and resonance donating. This combination makes halogens deactivating, but O, P directing.

See figure 17-5.

All directing effects are summarized on pg 337.

Effects of multiple substituents imply sum up the directing effects. Often the result is clear, but not always.
The orientation of substitution is also often clear.

However, mixtures are possible.

Activating groups are usually stronger than deactivating groups.

Strong activators that stabilize via resonance rank highest.

OH, OR, NRS

Moderate o,p directors - R, - X are next.

Meta directors last. See solved problem 1.

Iodel-Crafts Alkylation

Alkyl Halides

Alkylate the ring in the presence of Lewis acids.

It's a typical electrophilic aromatic substitution.

Carbocation is the electrophile.

Formation of carbocation.

Alternative carbocation sources may also be used, such as protonation of alkenes.

The F⁻ anion is a poor nucleophile, not too reactive towards the cation.
IMITATIONS OF FRIEDEL-CRAFTS ALKYLATION

1) WORKS ONLY WITH ACTIVATED RINGS
2) CARBONATION REARRANGEMENTS
3) AFTER ALKYLATION, RING IS MORE ACTIVATED, GIVING POLYALKYLATION PRODUCTS

OF THESE 3 LIMITATIONS ARE OVERCOME BY

FRIEDEL-CRAFTS ACYLATION
ITS VERY SIMILAR, BUT THE ELECTROPHILE IS THE ACYLIUM ION
IN ACYL GROUP IS R–C– O– NAMED BY DROPPING THE E FROM THE ALKANE NAME AND ADD - OYL

BENZENE → BENZOYL

MAKING ACYL GROUPS GET COMMON NAMES

H–C–O
CH3–C–O
FORMYL
ACETYL
PROPIONYL

WHEN AN ACYL GROUP IS BONDED TO A CHLORINE, ITS CALLED AN ACID CHLORIDE

FRIEDEL-CRAFTS ACYLATION IS THE STANDARD ELECTROPHILIC SUBSTITUTION
HE ELECTROPHILE (SIMPLISTICLY) IS THE ACYLIUM ION

\[ R–C–C\overset{0}{\longrightarrow}\overset{0}{\text{AlCl}}_3 \rightarrow R–C^+ + \text{AlCl}_4^- \rightarrow R–\overset{0}{C}–\overset{0}{\text{R}} \]

THE ACYLIUM ION IS RESONANCE-STABILIZED
SO NO REARRANGEMENTS R–C=O. ↔ R–C=O:

UD THE ACRYLATED PRODUCT IS DEACTIVATED TOWARD FURTHER SUBSTITUTION,
IE BULKINESS OF THE ACYLIUM COMPLEX OFTEN FAVORS PARA SUBSTITUTION

ACYLATION AND ALKYLATION ARE SUMMARIZED ON PB 759
FREQUENTLY THE PHENYL KETONE IS REDUCED TO THE ALKANE

\[ \overset{0}{\text{O}}–\text{CH}_2–\text{CH}_3\overset{0}{\text{Zn}}(\text{Hg}) \overset{\text{HCl}}{\longrightarrow} \text{CH}_2\text{CH}_3\text{CH}_2\text{Zn}(\text{Hg}) \]

THIS IS CALLED THE CLEMMENSEN REDUCTION

NOTE THAT THIS ALKYL BENZENE COULD NOT BE MADE BY ALKYLLATION
DUE TO REARRANGEMENT PROBLEMS
**DIAZONIUM SALTS**

Alkylamines react with nitrous acid to form diazonium salt

\[ R-NH_2 + NaNO_2 + HCl \rightarrow R-N^+NCl^- \]

Primary diazonium salts decompose to form carbocations \( R^+ \), which then either rearrange, eliminate H to form an alkene or undergo nucleophilic substitution.

Secondary diazonium salts form nitrosamines, one of the most potent classes of carcinogens known.

\[ R-N-N=O \quad \text{A nitrosamine} \]

The main usefulness of diazonium salts is with aromatic amines, which may be converted into a wide variety of functionalities after diazotization.

A summary of arylamine transformations:

\[ \text{Al} \rightarrow \text{Al}^+ \]

\[ \begin{align*}
\text{H}_2\text{O}^+ & \quad \text{Phenols} \\
\text{C}_2\text{Cl}(\text{Br}) & \quad \text{Al}-\text{Cl}(\text{Br}) \quad \text{Halides} \\
\text{C}_6\text{CN} & \quad \text{Al}-\text{C}≡\text{N} \quad \text{Nitriles} \\
\text{HOCl}(\text{H}) & \quad \text{Al}-\text{F} \quad \text{Halides} \\
\text{H}_2\text{PO}_2^{-} & \quad \text{Deamination} \\
\text{Al}^+ & \quad \text{Al}-\text{N}=\text{N}=\text{Al}^+ \quad \text{Diazobenzene}
\end{align*} \]

**Examples**

**Hydrolysis to the phenol**

\[ \text{NH}_2 \quad \text{(O)}  \quad \text{OH} \quad \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_4\text{Br} \]

1) \( \text{NaNO}_2, \text{HCl} \)  
2) \( \text{H}_2\text{SO}_4, \text{heat} \)

**Replacement by Cl, Br, CN** The Sandmeyer reaction

\[ \text{NH}_2 \quad \text{(CH}_3\text{)} \quad \text{(Cl, Br, CN)} \]

1) \( \text{NaNO}_2, \text{HCl} \)  
2) \( \text{CuBr} \quad \text{(Cl, Br, CN)} \)

This is a useful way to attach a new carbon to an aromatic ring

Once you have the new carbon on the ring, you can go on to modify it.
DIORE DIAZONIUM REACTIONS
REPLACEMENT BY F AND I

\[ \begin{align*}
\text{NH}_3 & \quad \xrightarrow{1) \text{NaNO}_2, \text{HCl}} \quad \text{I} \\
\text{NH}_3 & \quad \xrightarrow{2) \text{KI}} \quad \text{O} \\
\text{CH}_3 & \quad \xrightarrow{1) \text{NaNO}_2, \text{HCl}} \quad \text{F} \\
& \quad \xrightarrow{2) \text{HBF}_4} \quad \text{O} \text{CH}_3
\end{align*} \]

THIS IS THE BEST WAY TO GET F OR I ONTO AN AROMATIC RING.

DEAMINATION

\[ \begin{align*}
\text{NH}_2 & \quad \xrightarrow{1) \text{NaNO}_2, \text{HCl}} \quad \text{O} \\
& \quad \xrightarrow{2) \text{H}_3\text{PO}_4} \quad \text{O}
\end{align*} \]

AN AMINO GROUP MAY BE ADDED TO A RING TO ACTIVATE IT AND DIRECT SUBSTITUTION.
A GOOD EXAMPLE IS THE SYNTHESIS OF \[ \begin{align*}
\text{B}_2 & \quad \text{O} \\
& \quad \text{O} \text{CH}_3
\end{align*} \] FROM TOLUENE.

DIRECT DROMINATION OF TOLUENE GIVES A MIXTURE OF ORTHO AND PARA SUBSTITUTION.

\[ \begin{align*}
\text{CH}_3 & \quad \xrightarrow{\text{Br}_2, \text{FeBr}_3} \quad \text{CH}_3 \\
& \quad \text{CH}_3 \\
& \quad \text{O} \text{CH}_3 + \text{OTHERS}
\end{align*} \]

AN AMINO GROUP ACTIVATES AND DIRECTS P-TOLUIDINE.

\[ \begin{align*}
\text{CH}_3 & \quad \xrightarrow{\text{Br}_2, \text{FeBr}_3} \quad \text{CH}_3 \\
& \quad \text{NH}_2 \\
& \quad \text{N} \text{H}_2 \\
& \quad \text{O} \text{CH}_3 \\
& \quad \xrightarrow{1) \text{NaNO}_2, \text{HCl}} \quad \text{O} \\
& \quad \xrightarrow{2) \text{H}_3\text{PO}_4} \quad \text{N} \text{O} \\
& \quad \text{N} \text{O} \\
& \quad \text{B}_2 \\
& \quad \text{B}_2
\end{align*} \]

DIAZO COUPLING PRODUCES Azo DYES

\[ \text{AlN}_2^+ + \text{A}_1^- \text{H} \rightarrow \text{Al}^- \text{N=N-A}_1^- \]

THESE HIGHLY CONSOLIDATED SYSTEMS ARE STRONGLY COLORED USED IN TEXTILES.