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High pressure spectral chemistry of selected organic compounds

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HIGH PRESSURE SPECTRAL CHEMISTRY

OF SELECTED ORGANIC COMPOUNDS

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

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I am especially grateful to my wife, Sonja, and to our daughters Julie and Brenda who were a source of joy and understanding and support throughout this work. This work is dedicated to them.

INTRODUCTION

The basic idea for this study was fostered in a class taught
by Dr. H. Tracey Hall, in a discussion of isoelectronic systems (1).

An isoelectronic system consists of two or more molecules which
have the same average number of valence electrons. When the electro-
negativity difference (dX) between the atoms of a molecule is small, the
physical properties are very similar to other members of the system (2).
As an example let us consider the isoelectronic system consisting of
carbon, boron nitride (BN), beryllium oxide (BeO) and lithium fluoride
(LiF).

Observation of the elements with principle quantum number n=2,
illustrated in Figure 1, shows that carbon is the central element of the
series. Carbon's electronic configuration is $2s^2 2p^2$ which leads to
several hybridized configurations of which the most important in this
study is the sp^3 hybrid. Carbon in its natural uncombined state exists
in two forms, graphite and diamond. The diamond form has carbon bonded
to itself in a tetrahedral (sp^3) configuration. The bonding is covalent
and thus the carbon has an average of four electrons about each nucleus.
Carbon has an electronegativity of 2.5 but since in the diamond lattice
carbon is bound only to carbon there is no electronegativity difference
(dX=0) between adjacent atoms.

If we combine the elements on either side of carbon we would
obtain the compound BN. This grouping would have a total of eight
valence electrons. Three electrons from boron and five from nitrogen
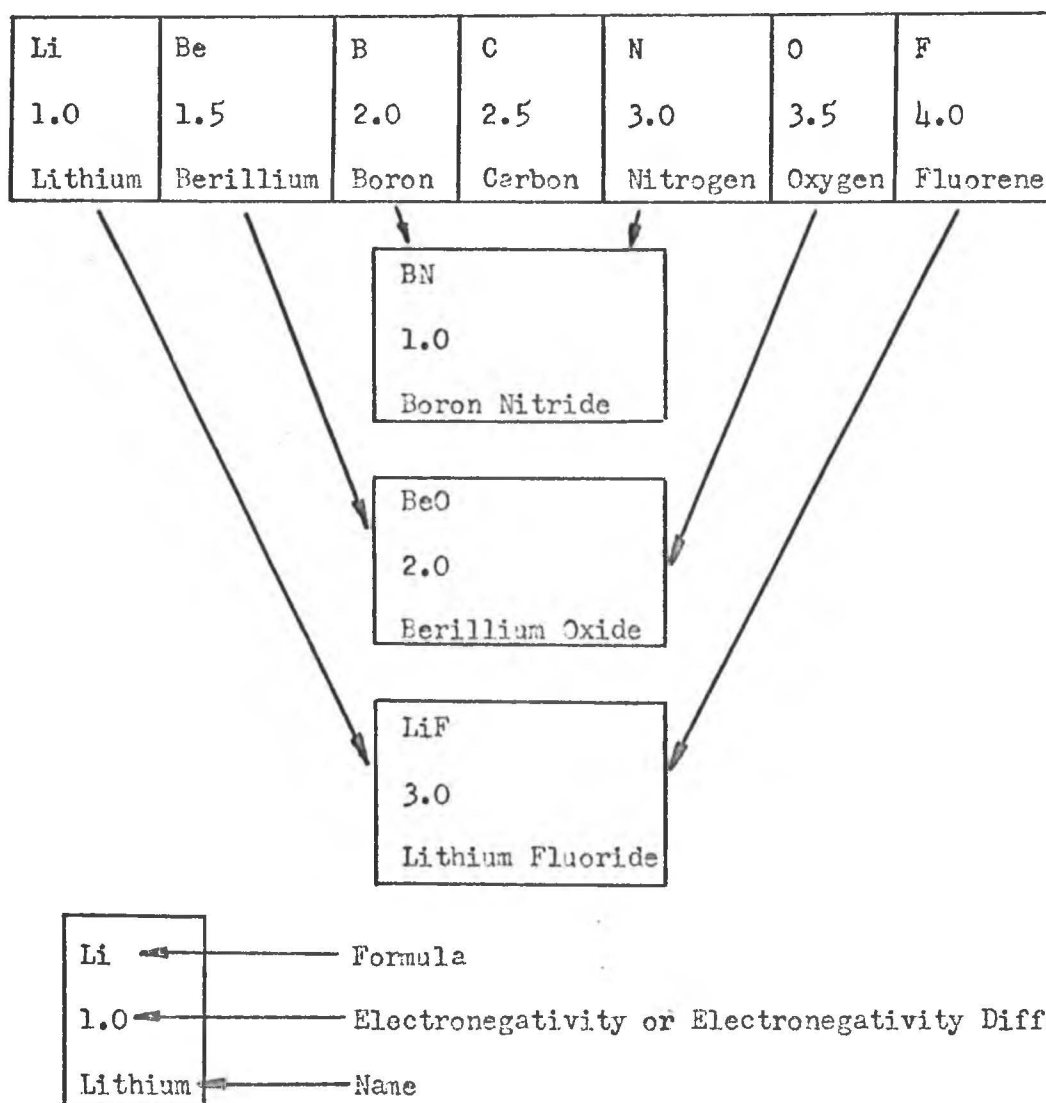
1

Figure 1: Elements of the First Period

making an average of four valence electrons per atom in the molecule.
The average atomic weight is 12.4, very close to that of carbon at
12.0. The electronegativities for boron and nitrogen are 2.0 and 3.0
respectively so the electronegativity difference of the adjacent atoms
in the molecule is small (dX=1.0).

This compound has long been known in an hexagonal, layer-lattice
form related to graphite. More recently it has been converted into the
tetrahedrally bonded form by means of high pressure and high temperature
in the presence of a catalyst (16). This form of BN imitates the
properties of diamond carbon quite well.

The next symmetrically oriented elements from carbon are beryllium
and oxygen. If we combined these we obtain BeO which in the same
manner as before has an average of four valence electrons per atom in
the molecule, and an average atomic weight of 12.5. The electronegativities
are such that dX=2.

The BeO compound is only known in one crystalline form - a
hexagonal wurtzite structure in which tetrahedral bonding prevails. It
is expected that the BeO bonding is somewhat more ionic than covalent,
and imitates the properties of diamond carbon only moderately.

The last member of the system would be LiF. With its dX=3.0,
and its bonding totally ionic, little imitation of diamond carbon is
observed. The compound is found only in the octahedrally coordinated
rock salt structure.

Organic molecules are said to be isoelectronic if they have the
same number of electrons and the same number of heavy atoms (3). "Heavy
atoms" mean, in this case, any atom other than hydrogen, helium, or lithium.

To illustrate, the molecules $H_2C=C=CH_2$ (allene), $H_2C=C=O$ (ketene), $HN=C=O$ (isocyanic acid), and $O=C=O$ (carbon dioxide), all have 22 electrons and three heavy atoms and are thus an isoelectronic system.

If by some alchemy process, a migration of a hydrogen proton into the nucleus of its attached heavy atoms could take place, the heavy atom would increase its atomic number by one and thus become an isotope of the next periodic element. The bonding pair of electrons would then become a spin paired set belonging to the new heavy atom and have their general location essentially unaltered. This alchemy is illustrated in Figure 2a for the carbon, nitrogen and oxygen transformations of the previously mentioned isoelectronic system.

It will be noted that the bonding electrons and the spin paired electrons in these molecules are all in the same general location with respect to the corresponding heavy atoms as is dictated by the Lewis-Langmuir octet rules (4)(5).

Physical similarities also arise in these organic isoelectronic systems. Obvious similarities for the above organic molecules are that the molecules are all linear, and the electron cloud distributions are almost identical. The C_3H_4 and N_2O isoelectronic molecules show similarities in their infrared spectra indicating very similar electronic structures (3).

Taking note of these spectral similarities, it was thought that if we took two isoelectronic molecules we might be able to induce a spectral similarity by applying pressure to one of them. The system trans-stilbene, azobenzene shown in Figure 2b was chosen. The stilbene crystal is colorless and if the isoelectronic equilbrium could be
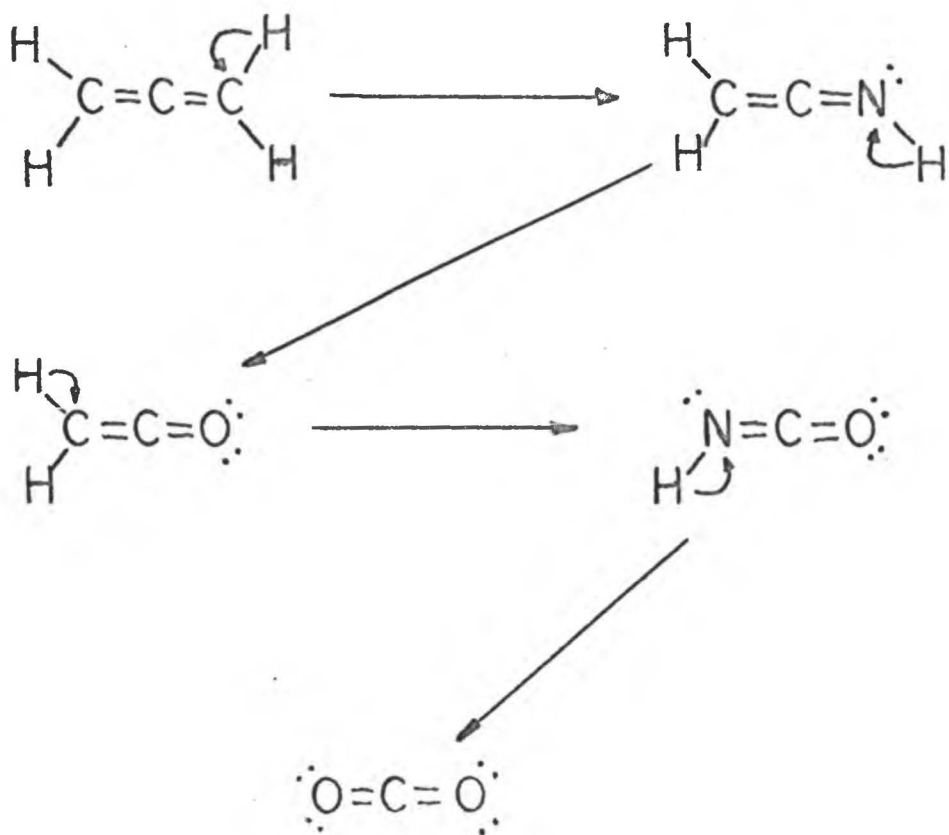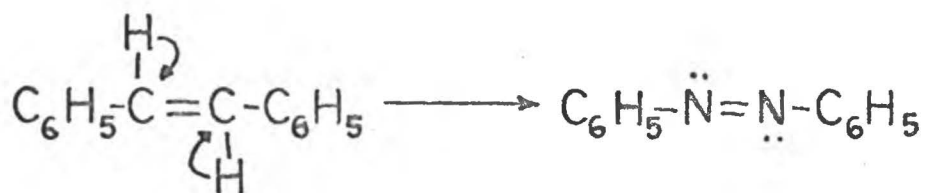
Figure 2a: Isoelectronic System

Figure 2b: Stilbene Azobenzene Isoelectronic Transformation

shifted by forcing the protons to migrate, theoretically, the azobenzene red color could appear by a chromophoric shift to the red end of the spectrum.

A diamond anvil press capable of achieving pressures in excess of 100 kilobars (kb) was supplied by Dr. William Bassett of the University of Rochester. The diamonds are used because they provide a convenient window for observation of the substance under pressure.

The colorless stilbene was pressed for the first time in April of 1968. Using a microscope to observe the crystal, two color changes or shifts were noted as the pressure was increased. The first was the appearance of a yellow color, then a red colored area appeared in the center portion of the diamonds.

Description of high pressure techniques and results in the literature involve several units of pressure. Table 1 (6) reports the most common units and their conversion factors. In this paper the kilobar (kb) will be used exclusively.

It has been observed that the optical absorption band of lowest energy in crystals of hydrocarbons moves to lower energy with increasing number of rings (7). An example of this is the series benzene, naphthalene, anthracene, tetracene and pentacene as illustrated in Table 2 (19). The explanation of the cause is that the pi electrons are conjugated around an increasingly longer path length.

Kohn in his early work synthesized an extremely interesting series of compounds (8). The compounds are the series $C_6H_5-(CH=CH)_n-C_6H_5$ where n varies from 1 to 19. These were the first hydrocarbons synthesized with an orderly color series, and proved that hydrocarbons have color. The color changes gradually from white (colorless) to
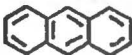
TABLE 1

UNITS OF PRESSURE MOST COMMONLY USED

	bar[a]	atm[b]	kg/cm^2
1 atm	1·013250	1	1·033227
1 bar	1	0·986924	1·019716
1 kg/cm^2	0·980665	0·967842	1

[a] bar is equal to 10^6 $dyne/cm^2$

[b] atm is the normal atmosphere now defined as 1,013,250 $dyne/cm^2$

TABLE 2

BENZENE THROUGH TETRACENE SPECTRA SERIES

Name	Formula	E_{max}	Lowest Energy Absorption Peak
Benzene		2550	2690
Naphthalene		2200	3120
Anthracene		2530	3745
Tetracene		2790	4730

yellow to orange to red to deep red as n increases from 1 to 12. This series also has a conjugated system of pi electrons and shows the red chromaphoric shift with increasing path length. Some of these compounds and their properties are shown in Table 3 (9).

It will be noticed that stilbene is the first member of this series. Since stilbene had a red shift under pressure it was thought that the succeeding members might also have a similar shift. In other words the application of pressure would have the same result as the increase of n, that is the color changes progressively toward red. It was observed that the color change did occur and that when succeeding member of the series were tried that less and less pressure was required for the shift.

The color change was apparent by simple visual observation. To see if there was any heat of transformation or resistance change at the transformation to accompany the color change, measurements using the tetrahedral press were taken.

TABLE 3

ETHYLENE HOMOLOGUES

| NAME	STRUCTURAL FORMULA	CRYSTAL COLOR	MELTING POINT*
trans-1,2-Diphenylethylene (Stilbene)	$C_6H_5-CH=CH-C_6H_5$	Colorless (white)	124-126
1,4-Diphenyl-1,3-butadiene	$C_6H_5-(CH=CH)_2-C_6H_5$	Pale Yellow	151-153
1,6-Diphenyl-1,3,5-hexatriene	$C_6H_5-(CH=CH)_3-C_6H_5$	Lemon Yellow	199-203
1,8-Diphenyl-1,3,5,7-octatetraene	$C_6H_5-(CH=CH)_4-C_6H_5$	Chrome Yellow	235-237
1,10-Diphenyl-1,3,5,7,9-decapentaene	$C_6H_5-(CH=CH)_5-C_6H_5$	Orange	258-261

APPARATUS

The high pressures required for this study were achieved by the use of a double ended, opposed diamond anvil press (see Figure 3 and 4) built by Dr. William Bassett of the University of Rochester (10). The press is designed in such a manner as to enable an excess of 100 kb to be generated. The configuration permits visual observation of the material under investigation.

To load the press either a single or several crystals of the compound of interest were placed on the face of the diamond in the lower holding block (B in Figure 3), which was mounted in the body (C in Figure 3), then the top holding block (D in Figure 3) was screwed into placed and bottomed out. The lower holding block was then raised by twisting the backup ring (A in Figure 3) counterclockwise, utilizing the specially designed wrenches shown with the assembled press in Figure 4. The design permits the diamonds to be forced together with no twisting moment on the impinging faces. Care must be taken to insure the opposing faces are parallel or failure of one or both diamonds may occur.

The entire face of the smaller anvil in the lower holding block must be covered with the material being studied, in order for a meaningful spectrum to be recorded. Also the thickness of the sample must be such that enough light is transmitted. This was accomplished

11
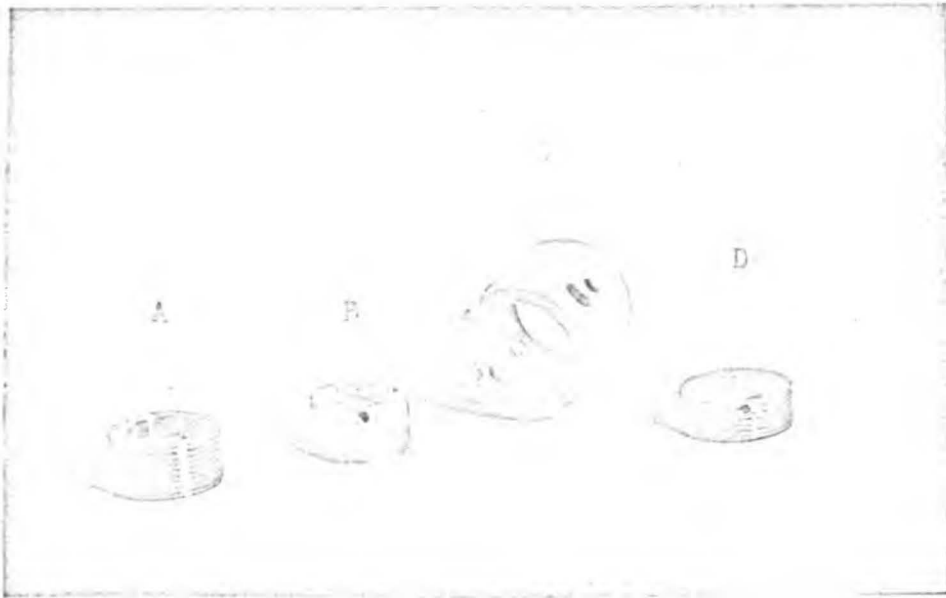
A- Back-up ring

B- Lower holding block (small diamond in center)

C- Press body

D- Upper holding block (large diamond in center)

Figure 3: Parts of the Diamond Anvil Press
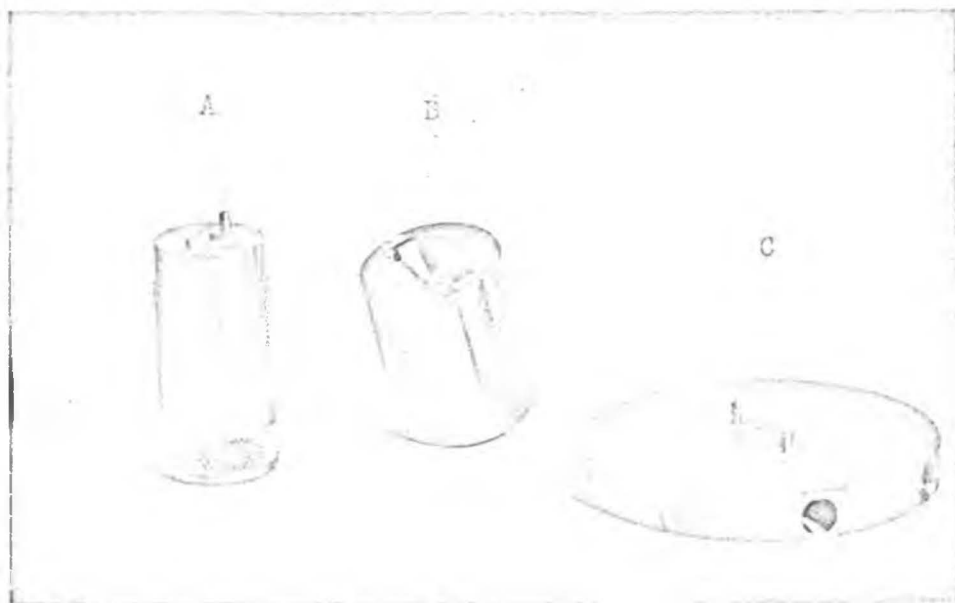
A- Upper holding block wrench

B- Assembled press

C- Back-up ring wrench

Figure 4:   Assembled Diamond Anvil Press With Tools

basically by trial and error.

The spectra were obtained using a Beckman DK-2 spectrophotometer, an automatic recording, double beam instrument. A special holder and reference cell was built to adapt the press to the instrument.

For larger samples the multi-anvil tetrahedral press, with anvil guide device, developed by H. T. Hall, was used (see Figure 5) (11) (12). The four hydraulic rams are rated at 200 tons (force) capacity, capable of developing pressures in excess of 100 kb with the 1/2 inch anvils.

The sample holder for the tetrahedral press were made of pyrophyllite, a hydrated aluminum silicate. The sample was held inside a boron nitride tube with end caps (labeled 4 Figure 6) which in turn was inside a tube and end caps of graphite (labeled 3 Figure 6) which fits into the hole in the pyrophyllite tetrahedron (labeled 1 Figure 6). The molybdenum tabs were used for electrical leads to the sample.

For the resistance measurements, the sample was packed into a hollow silver chloride pellet and a short length of platinum or silver wire was forced into the ends of the sample. The wires insured good electrical contact between the sample and molybdenum tabs. This configuration was placed into the hole in the pyrophyllite tetrahedron replacing the boron nitride and graphite and capsule.

The Weston Megohm meter was used for the resistance measurements. The meter was connected to two electrically insulated anvils, then the sample holder was mounted properly to make a complete series circuit as the anvils advanced and made contact.

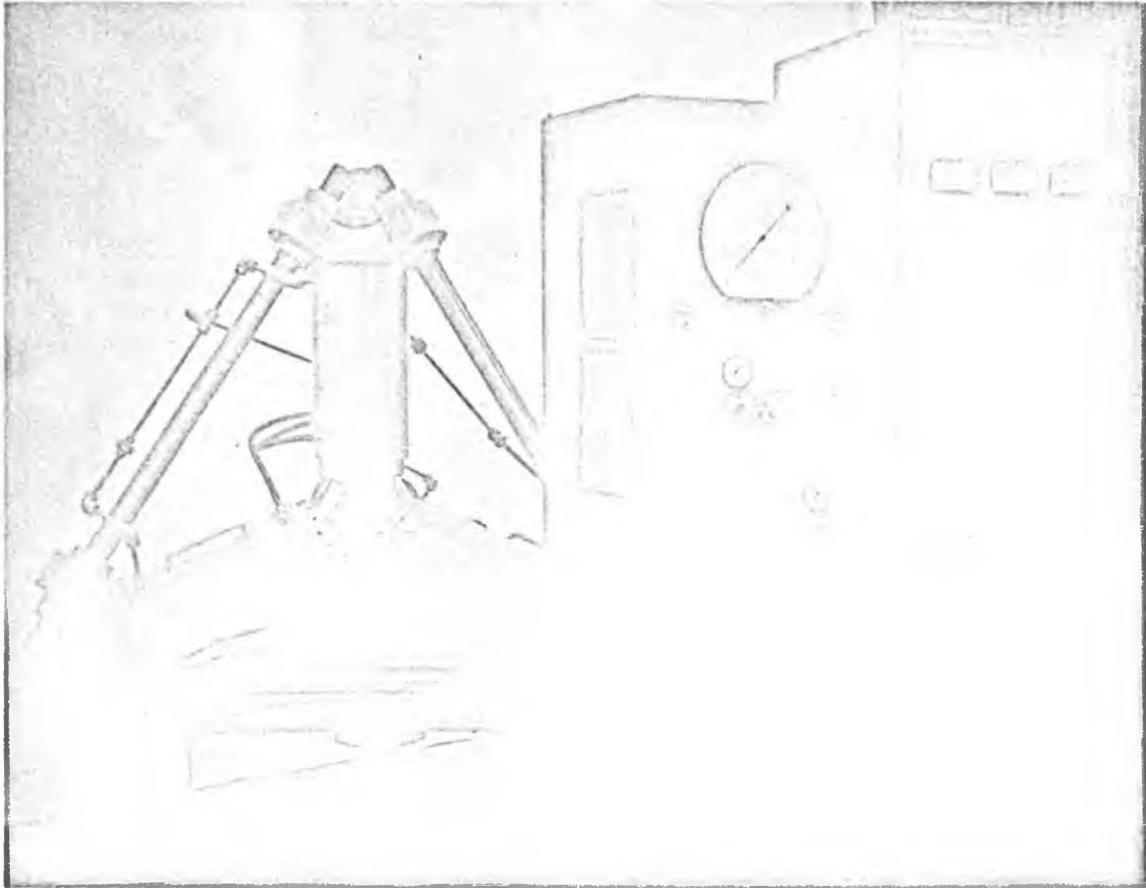The pyrophyllite tetrahedrons were either 0.94 in or 0.72 in.

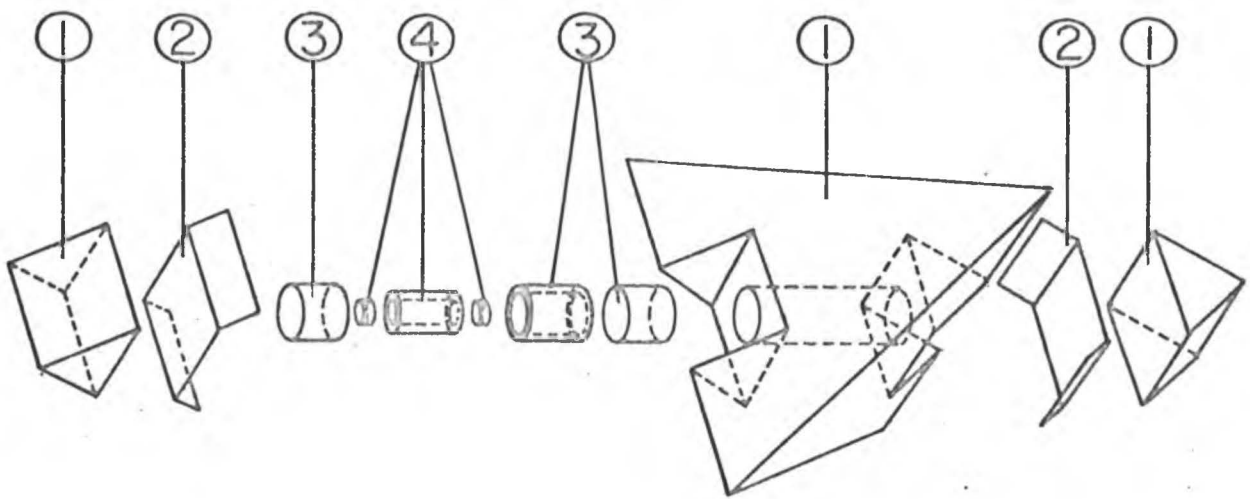Figure 5: Tetrahedral Press and Control Panel

Figure 6: Exploded Tetrahedron with Interior Configuration

on an edge depending on whether the 0.75 in. or 0.5 in. (edge length) anvils were used in the press. The slots were 0.251 x 0.230 in. or 0.02 in. thick respectively. The graphite tubes were 0.125 in. O.D. and 0.140 in. long. The boron nitride tubes were 0.036 in. O.D. and 0.100 in. long. The end caps had the same O.D. and were 0.02 in. thick.

After the desired sample configuration was assembled, a strip of paper was glued to one edge of the tetrahedron and the outside was painted with a Fe_2O_3 and methanol slurry which helped to optimized the internal pressure with minimum ram pressure. This complete assembly was then baked at 110° C for at least one hour.

To mount the sample on the press the strip of paper was taped to one anvil with the molybdenum tabs alligned for proper electrical contact. The rams were then advanced until contact was made on all faces. The air pump was then used to slowly advance the rams, this caused the pyrophyllite of the sample to extrude out between the anvils to form gaskets which help to support and seal the sample in place (15). The pressure was increased slowly until the main gasket forming region was passed and then increased rapidly to the desired pressure. For resistance measurements the pressure was increased slowly for the entire experiment to optimize the internal equilbrium.

The pressure calibration curves shown in Figure 7 were determined by Webb for the 0.5 in. anvils (13) and by Miller and Eatough for the 0.75 in. anvils (14).
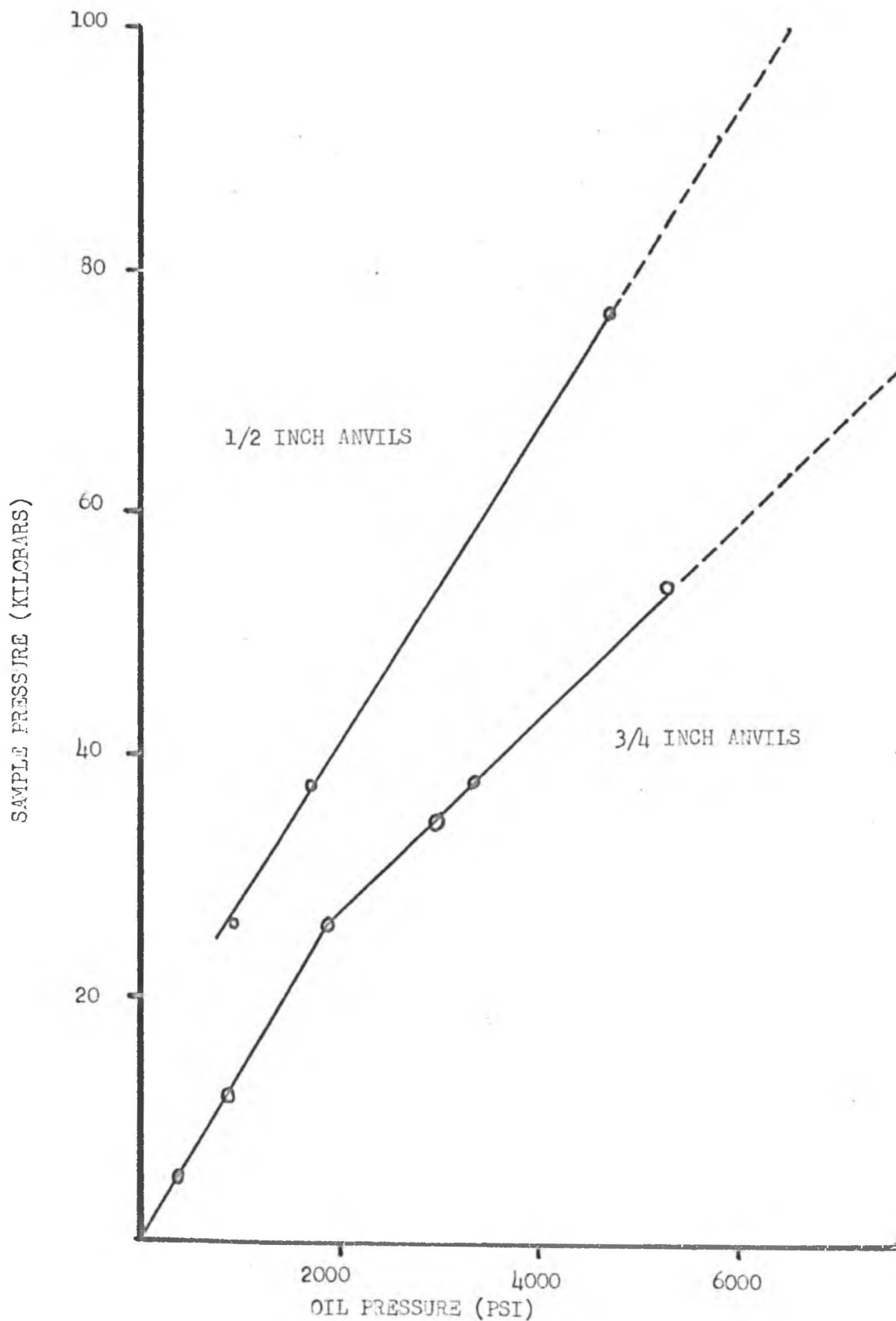
Figure 7: Pressure Calibrations

SPECTRAL STUDIES

The sample under investigation was put in the press and squeezed between the diamonds. The sample was observed at all times under a microscope. There is a pressure gradient across the face of the diamonds. The pressures to which the sample is subjected drop from the maximum value at the center of the anvil area to atmospheric pressure at the edge of the anvils. If a single crystal phase is present, the rate drop approximates a parabola (17). If two phases are present, a high pressure phase in the center and a surrounding low pressure phase, the pressure gradient is altered to a shape like a composite of two parabolae, as shown in Figure 8.

In order to obtain meaningful spectra the entire field should have the same appearance. This is sometimes difficult to achieve, due to the pressure gradient, especially at higher pressure.

The ideal technique would be to have a beam condenser pinpoint the spectrometer beam to the high pressure center area where the high pressure phase could be monitored independently. No suitable condenser was available at the time of this study. The next technique was to try and form a mask to block out the low pressure area. These attempts were also fruitless. Therefore if a uniform field could not be achieved and the limit of the press was judged to have been reached the spectrum was recorded and a note made that the optimum field was achieved.

The Beer-Lambert law for optical absorption can be formulated by

19
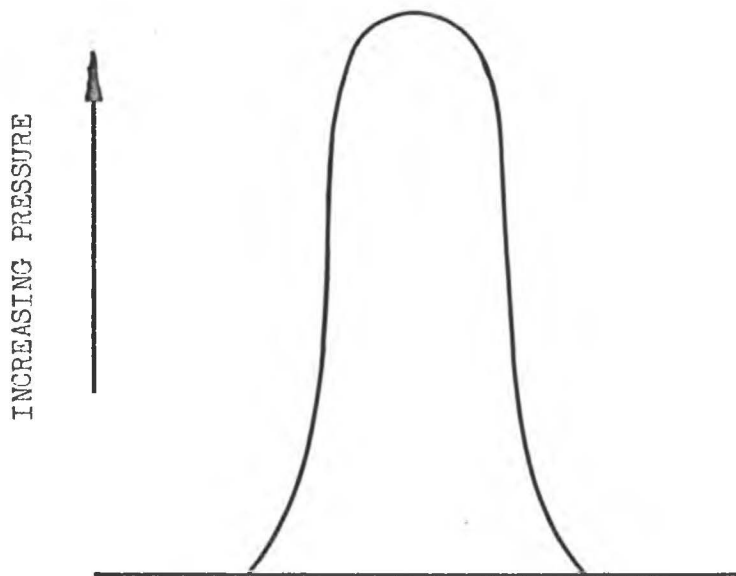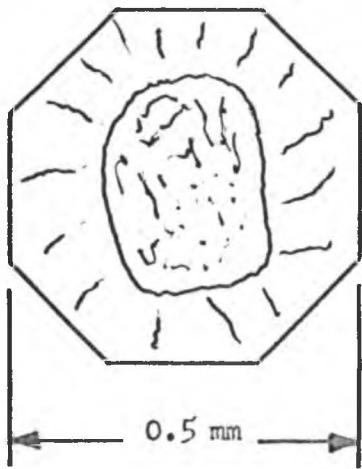
0.5 mm

INCREASING PRESSURE

Figure 8: Pressure Curve on Diamond

the relationship:

$$a = \frac{A}{cl}$$

A = absorbance

a = molar extinction coefficient

c = molar concentration

l = path length in centimeters

In the case of a solid like in the diamond press the concentration can
be determined by the relation:

$$c = \frac{1000 \cdot p}{M.W.}$$

p = density of the sample

M.W. = molecular weight

This is based on the assumption of 100% purity of the crystal. As will
be noted, the density of the compound at the given pressures is needed.
The data for these compounds were not available. Also we were unable
to measure the cell thickness reliably because of the nonreproducible
quantity of samples between the anvils. It was noted that a small
difference is sample thickness made a great deal of difference in the
quantity of light transmitted. Therefore in this study we report only
the observed data for the several compounds.

The pressure calibration of the diamond press was semi-empirical.
Silver iodide used for the calibration has phase transitions at 5 kb and
at 100 kb, indicated by the appearance of a distinctive yellow area in
both cases (10). The "feel" for these pressures was achieved through
experience and as such no great deal of accuracy is claimed for the

pressure reported and are open to subsequent correction.

The spectra for stilbene are shown in Figure 9. The curve indicated yellow was taken at about 5 kb and appeared to be a creamy yellow. The curve marked orange is taken at about 45 - 64 kb and looked dark yellow with pimples of red in the center. The red curve was obtained at about 75 - 90 kb when approximately 85% of the field was red and 15% was yellow. The separation, I believe, is not as great as in shown because the sample was run for the first two curves and then thickened to achieve the high pressure of the red state. At that point one of the diamonds failed.

The spectra for 1,4-diphenyl-1,3-butadiene are shown in Figure 10. The color of this compound at atmospheric pressure is lemon yellow. The curve marked yellow is a creamy yellow at about 5 kb. The orange curve was taken at about 15 - 30 kb and the red was taken at about 40 - 60 kb.

Since 1,6-diphenyl-1,3,5-hexatriene is already yellow the spectra were taken at 5 kb and about 25 - 35 kb to show the yellow and red state (see Figure 11).

1,8-Diphenyl-1,3,5,7-octatetraene is chrome yellow so the two spectra taken were at 5 kb and 15 - 20 kb at the yellow and red state (see Figure 12).
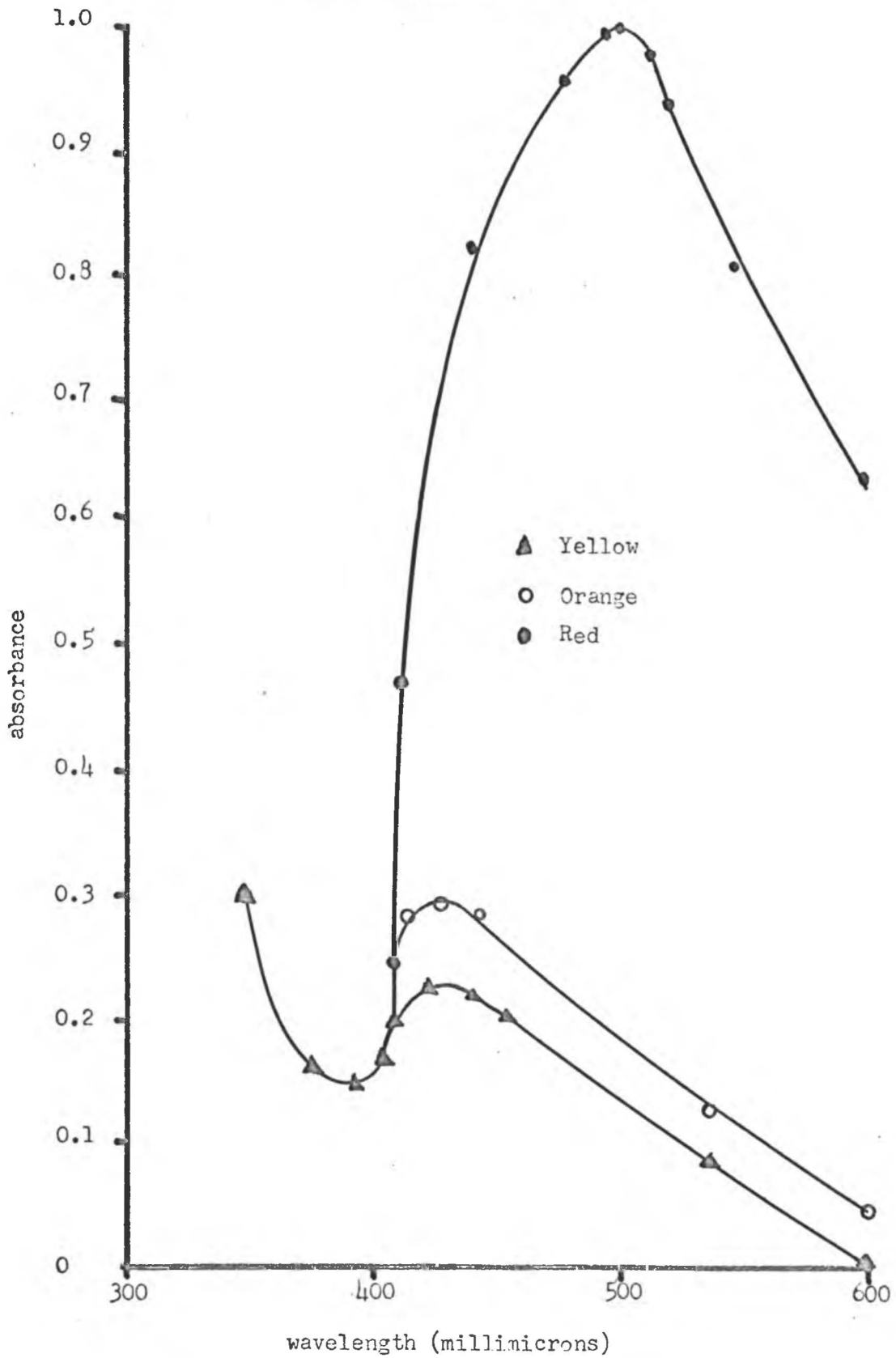
trans-Stilbene

Figure 9: Pressure Spectra of Stilbene

1,4-Diphenyl -1,3-Butadiene
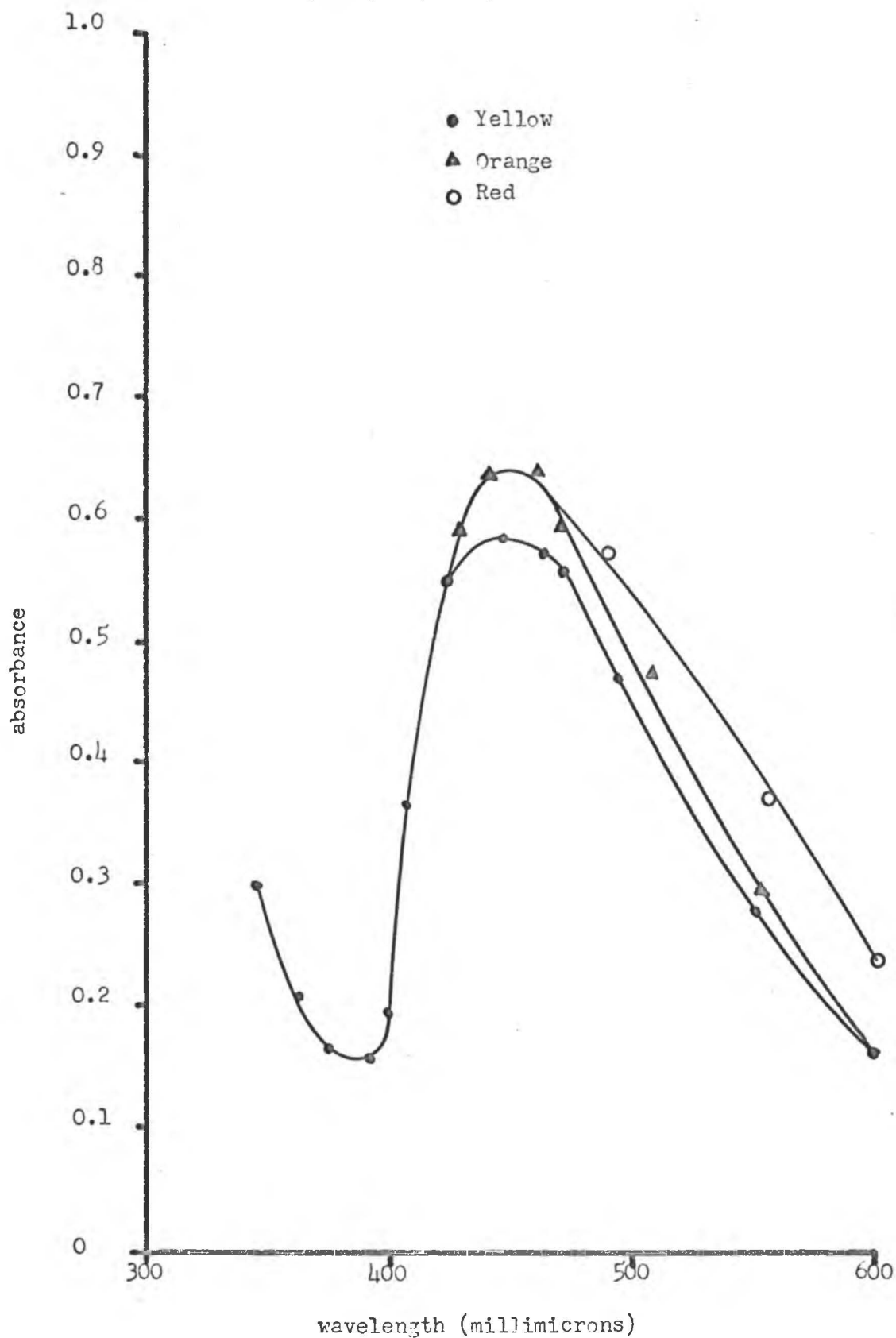

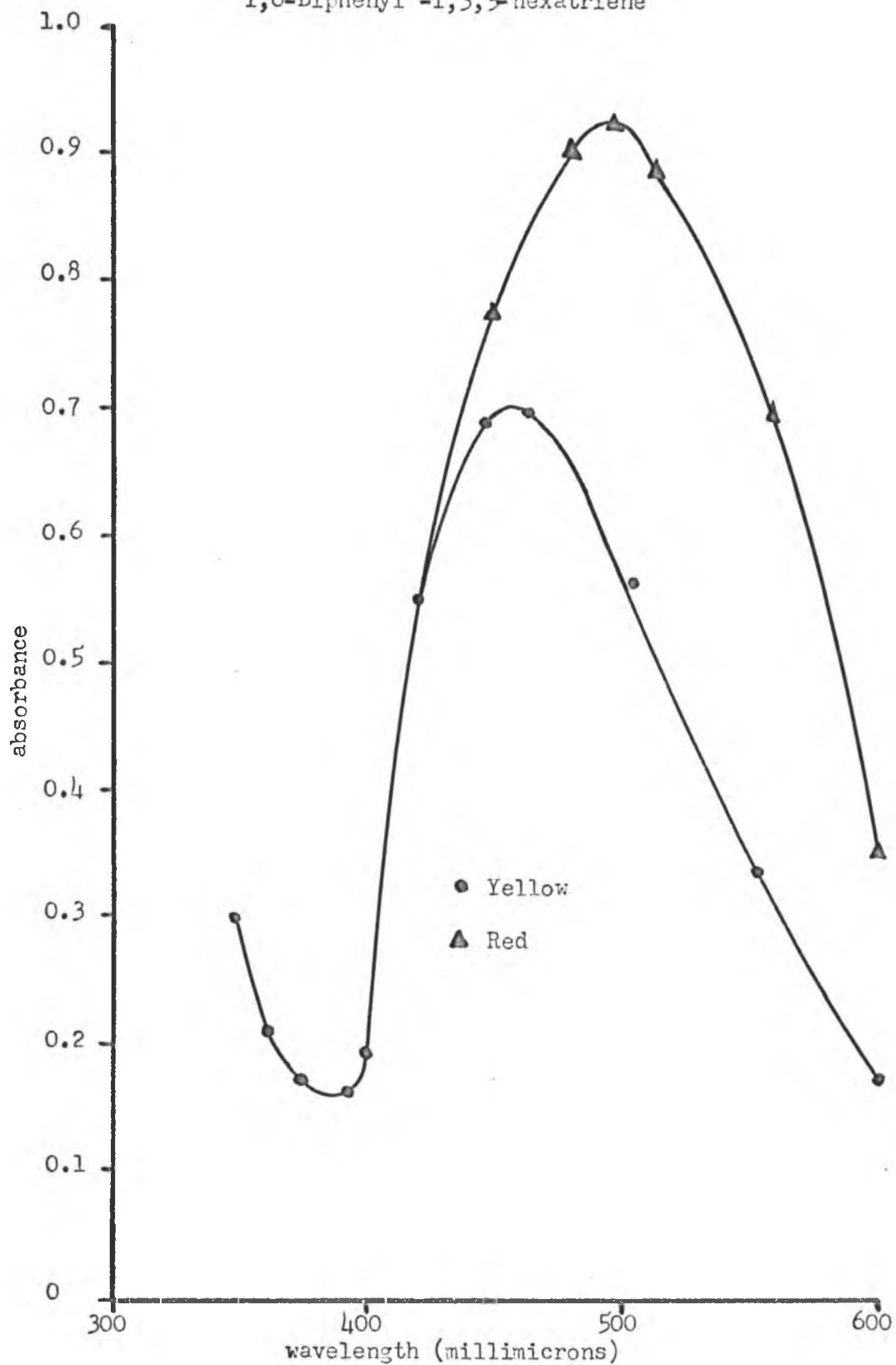Figure 10:   Pressure Spectra of 1,4-Diphenyl-1,3-butadiene

Figure 11: Pressure Spectra of 1,6-Diphenyl-1,3,5-hexatriene

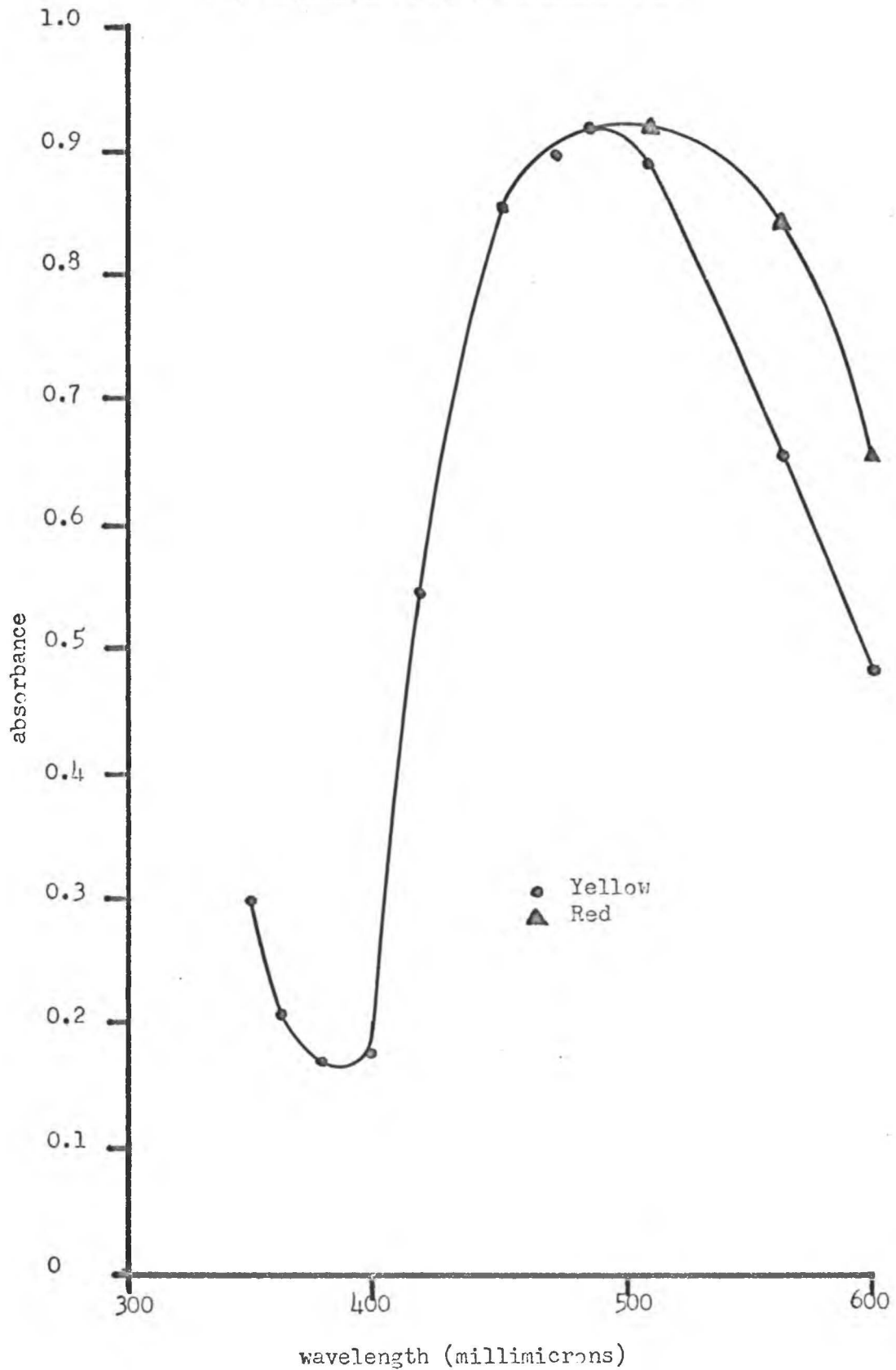1,8-Diphenyl -1,3,5,7-octatetraene

Figure 12: Pressure Spectra of 1,8-Diphenyl-1,3,5,7-octatetraene

SUPPLEMENTAL STUDIES

It was thought that there might be a change in resistance to correspond with the spectral changes (13). The resistance cell arrangement was placed in the press and measurements taken at every 200 pounds oil pressure increase. The results for stilbene and 1,4-diphenyl-1,3-butadiene are shown in Figure 12. The results showed no sharp resistance change to correspond with the spectral change. There was a sharp change but it came at a pressure lower than the color change. After the maxima is reached the compound's resistance decreased or became more metallic as the pressure increased.

One interesting phenomena observed was that every run had a blow out at the same point as the pressure decreased. This lead us to believe there was possibly a reversion pressure which could possibly be monitored as a differential temperature change (14).

A differential thermocouple was placed in the sample as described and the pressure was increased (12). The signal was put through an amplifier and the absolute and differential temperatures were monitored.

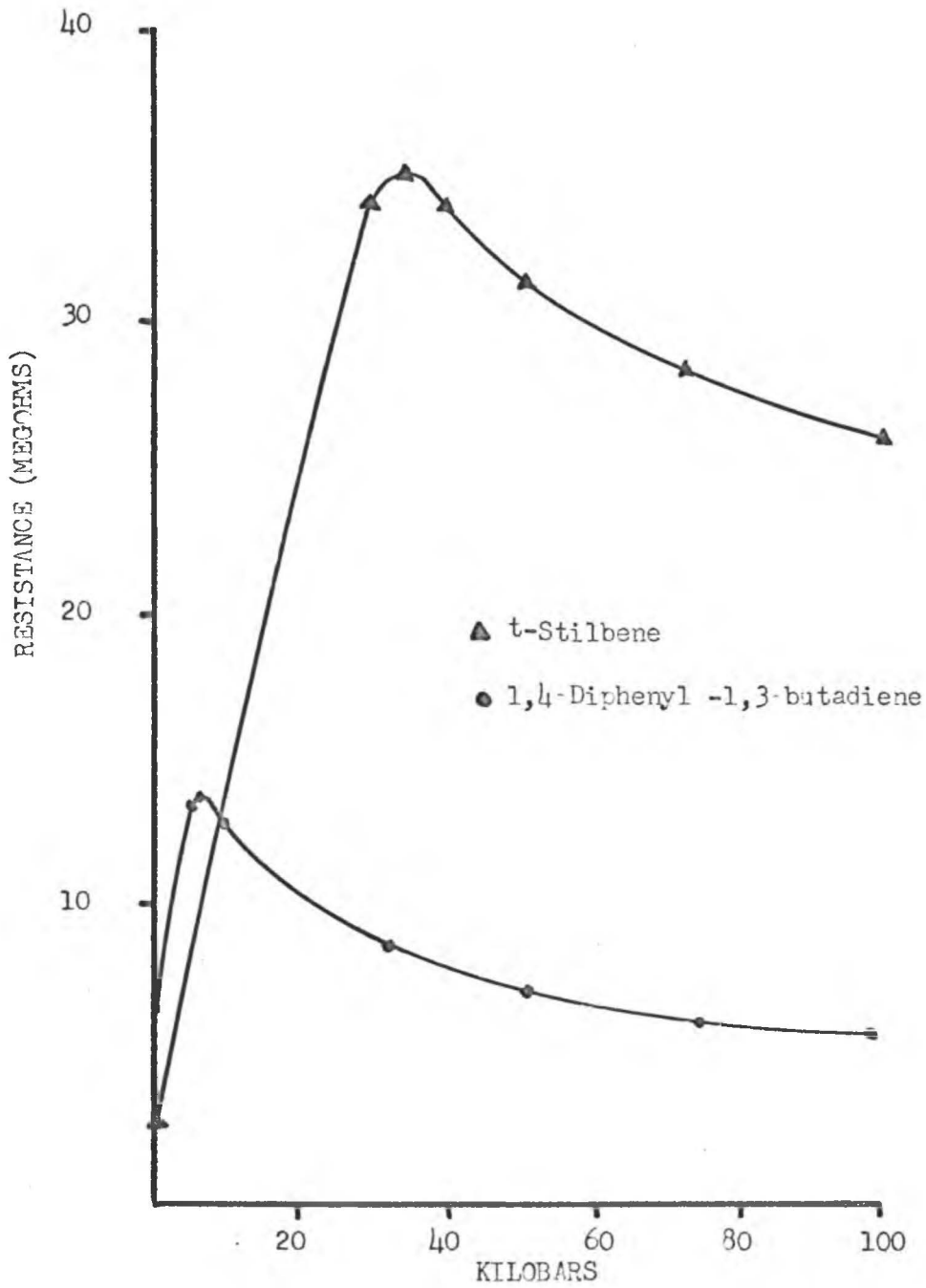The sample was cycled several times but no change was observed.

Figure 13: Pressure versus Resistance Curves

DISCUSSION

It is very tempting to attribute the color transformations solely to the isoelectronic transitions described in the introduction. The stilbene-azobenzene pair seems to establish at least a basis for this theory. The 1,4-diphenylbutadiene compound, if it followed along this line of reasoning, would form a compound with four conjugated nitrogen atoms between the two phenyl groups. This molecule, however, has not been isolated as yet at any pressure (24). If it could be formed, it most likely would be unstable. In dye chemistry is found a close relative of this compound, 1,3-diphenyltriazene, and it is deep red (23). This indicates that a conjugated chain of nitrogen atoms produces a red color. As the carbon chain length grows the transformed high pressure nitrogen compound would predictably be unstable, but would likely have a red color.

The most likely transformation, however, is that a high pressure polymorph or polymer is formed. One possible mode of accomplishing this is that the molecule was forced into a more compact crystal lattice which favored a polymer or polymorph form. This would tend to bring the different types of electron clouds in closer proximity which effectively increases the pi electron path length. This reasoning would seem to be supported by the same increased pi electron path length theory as discussed in the benzene to pentacene

29

series.

Cram (20) has studied the spectra of a series of compounds
which may be analogous to several high pressure configurational
situations. The paracyclophanes of type I and II in Figure 14 were
shown by Cram to have a spectral shift to shorter wavelength as m
and n decreased. This forces a cis configuration upon the ethylene
groups, while also bringing the phenyl groups closer together.
Paracyclophanes of type III show a bathochromic change when m=n
is decreased from 5 to 2. Thus, phenyl groups of separate molecules
being forced together cause a shift toward the red. It was calculated
that the shift occured when the phenyl groups were forced closer
than 3.4 Å.

It has also been shown (21) that when a cis bond is introduced
into a polyene chain the spectra shifts to shorter wavelength. This
is seen in cis and trans-stilbene where the cis is the shorter wave-
length specie, and in longer chained members of this series where
there is only one cis bond in the molecule.

Now let us consider the possibilities of inter and intramolcular
interactions of our molecules. When the more compact crystal is formed,
interactions of the following types are most likely: (1) intramolecular
interaction of the terminal phenyl groups, (2) intramolecular interaction
of the ethylene and phenyl groups, (3) intramolecular interaction of
an ethylene with another ethylene group, (4) intermolcular interaction
of two phenyl groups, (5) intermolecular interaction of two ethylene
groups or (6) intermolecular interaction of an ethylene group with a
phenyl group. The interaction spoken of could be either an actual bond
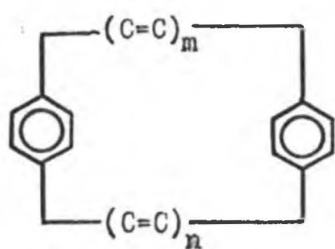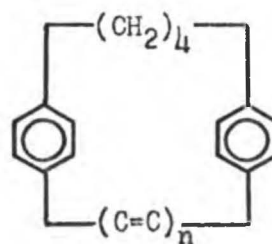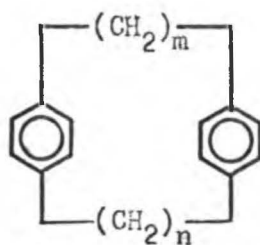
Figure 14: Paracyclophanes

being formed or simply the electron clouds being forced closer together causing some electronic mutation.

In order for any kind of intramolecular interaction to take place the ethylene groups would be forced into a cis configuration. However, we disucssed earlier that a cis bond or a configuration like the type I or II paracyclophanes cause the opposite effect than that observed at high pressure. Intermolecular interaction on the other hand effectively lengthens the pi electron path length or causes an effect like that of the type III paracyclophanes which support what we see at high pressures.

In conclusion, let us compare degrees of likelyhood. It is more likely that a molecular change takes place than an atomic change, simply because of the difference in molecular and atomic distances involved. It is also more likely that these molecular changes are intermolecular rather than intramolecular, as indicated by the above arguments.

It is entirely possible and most probable that more than one interaction takes place, but at this point of the study no quantitative statement can be made.

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HIGH PRESSURE SPECTRAL CHEMISTRY

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ABSTRACT

The series of compounds indicated by the formular $C_6H_5-(CH=CH)_n-C_6H_5$ change in color from white (colorless) to yellow to orange to red to deep red as n increases from 1 to 12. Stilbene is the first compound of this series (n=1). Under pressure, exerted by a diamond anvil press, stilbene can be seen to change color from white to yellow to red as increasing pressure is applied. Similar color changes are observed for the compounds where n=2,3, and 4 when subjected to similar pressure. This study records and reports the spectra versus pressure for these compounds.