JOURNAL OF SOLID STATE CHEMISTRY 3, 550–563 (1971)

Solid State Reactions in Organic Crystals at Very High Pressure*

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Received March 19, 1971

Studies have been made of the chemical reactivity of organic solids to pressures of 350 kilobars. The products have been recovered in milligram quantities and have been, in some degree, characterized. The systems studied include, acenaphthalene, a hydrocarbon which is quite reactive at one atmosphere, pentacene, a relatively unreactive hydrocarbon, and electron donor acceptor complexes of tetracyanoethylene with several hydrocarbon donors.

At 90 kilobars acenaphthalene polymerizes to a material which is very much like the thermal product made at one atmosphere and 100°C in the melt. At 255 kilobars acenaphthalene (or thermally produced polyacenaphthalene) reacts to form a highly insoluble polymer with a somewhat different infrared spectrum from the lower pressure polymer.

Pentacene reacts at 350 kilobars to form a product with distinctly altered electronic and infrared spectra as well as modified sublimation properties. It appears that it undergoes transpolymerization to a new kind of product. The mechanism of polyacene reaction is considered and a model proposed which accounts for the varying reactivity of different polyacenes.

The electron donor-acceptor complexes of tetracyanoethylene react at 90 kilobars to form large and apparently complex polymers.

A series of studies of the electrical resistance of aromatic hydrocarbons and their electron donor-acceptor complexes to pressures of 500 kilobars (*1*, *2*), showed unexpected irreversible behavior at very high pressure. This was presumed to be associated with chemical reactivity. However, since the samples were in the order of 0.1 milligrams, and very difficult to keep free from contamination, very little in the way of product characterization was possible.

In this research, we used the basic supported taper high pressure electrical resistance cell (*3*, *4*), with pyrophyllite support, modified to give larger volumes of product. Using the dimensions of the original design (flat 0.09 in. diameter, inside ring diameter 0.045 in., height of ring 0.0135 in.) but filling the entire ring with the product to be studied, we could obtain pressures of 350 kilobars on a sample of 0.6 milligrams. With a flat 0.130 in. in diameter, inside ring diameter 0.090 in. and ring height 0.027 in., we could obtain pressures of 260 kilobars on a sample of 2–3 milligrams.

The calibration involves measuring change of electrical resistance with pressure. The materials used in calibrating the large volume apparatus were lead, which undergoes a phase transition at 130 kilobars; potassium - tetracyanoquinodimethane (1:1) complex (potassium-TCNQ), which exhibits a minimum at approximately 112 kilobars and an abrupt change in slope at 200 kilobars; tetracyanoethylene-perylene (1:1) complex (TCNE-perylene) which exhibits a change in slope at about 130 kilobars and has a minimum at approximately 185 kilobars; and *p*-phenylenediamine-bromanil (3:1) complex, which levels at about 210 kilobars and has a linear region centered between 215 and 225 kilobars. All of these points were established in previous electrical resistance work (*1*–*3*). However, they are corrected for the recently revised pressure calibration based on X-ray diffraction data (*5*). It was felt very desirable to use organic materials in calibration so that they would be near the compressibility of materials used in the actual studies, even if they are not so well characterized as some metals. It is of interest that above about 120 kilobars the pressure was essentially linear in the logarithm

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* This research was supported in part by the U.S. Atomic Energy Commission under Contract AT(11-1)-1198.

of the applied force. This behavior has been observed for the high pressure region in other versions of the tapered piston cell. The procedure was to calibrate each batch of pyrophyllite pellets by two or three runs with a marker, and then to run with the pure sample in the center.

In this paper we present results for three types of materials, two hydrocarbons, and one class of electron donor-acceptor complexes. Acenaphthalene is a hydrocarbon which undergoes a variety of reactions at one atmosphere. Pentacene is a relatively unreactive hydrocarbon at one atmosphere. The complexes of tetracyanoethylene with perylene and naphthalene are reasonably characteristic of electron donor-acceptor complexes.

The acenaphthalene was from Aldrich Chemical Company. It was fractionally recrystallized ethanol as the picric acid complex. Commercial pentacene from Rütger-werke-Aktiengesellschaft was purified by two fractional sublimations. The TCNE, naphthalene, anthracene, and perylene were available in purified form from previous work in this laboratory. High pressure optical absorption studies were made on several of the reactants and products. The apparatus is essentially the same as that which has been previously described (*4*, *6*).

Acenaphthalene

Acenaphthalene undergoes a number of reactions at lower pressure. Dziewonski demonstrated that it can be dimerized photochemically (*7*, *8*), that it can be polymerized by heating above the melting point at 110°C (*9*), and that at 300°C it yields small amounts of dekacylene and fluorocyclene (*9*). A number of investigators have demonstrated that it could be polymerized by other methods including X-ray and radiochemical techniques in the solid state. Bradbury, Hamann, and Linton (*19*) polymerized it in the solid state at 50 kilobars using Bridgman anvils.

TABLE I

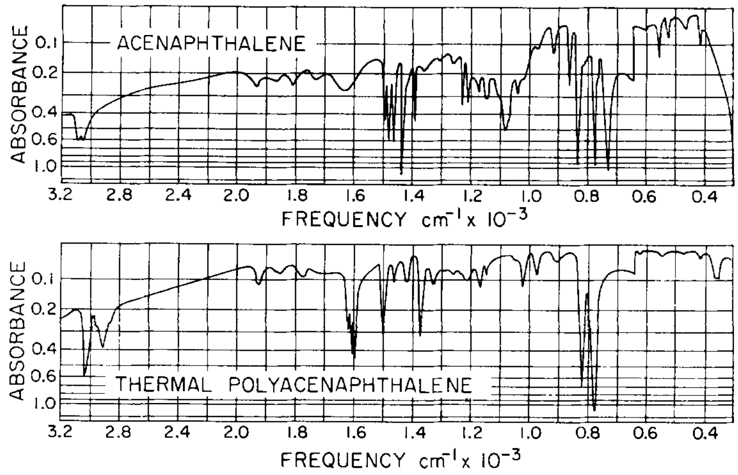
CRYSTAL STRUCTURES OF ACENAPHTHYLENE (*20*)

At room temperature	
Space group:	Pbam or Pba2
	$a = 7.71 \pm 0.05$ A
	$b = 7.86 \pm 0.05$ A
	$c = 14.01 \pm 0.05$ A
	$Z = 4$
At temperatures below −130°C	
Space group:	P2, nm
	$a = 7.65 \pm 0.05$ A
	$b = 7.80 \pm 0.05$ A
	$c = 27.90 \pm 0.15$ A
	$Z = 8$

Studies on the crystal structure of acenaphthylene have been undertaken by Welberry (*20*). His work indicates that acenaphthylene has a disordered structure at room temperature, but that below −130°C the disorder completely disappears yielding a crystal structure which he has been able to resolve. The lattice parameters of the two crystal structures are listed in Table I. Most of what is known about the room temperature structure has been inferred from the low temperature structure. The structure below −130°C consists of four repeating layers in which the layers at 0 and 1/2 c contain molecules inclined at about 20° to the b axis whereas the layers at 1/4 c and 3/4 c are inclined at about 20° to the a axis. The molecular mirror planes of the molecules at 0 and 1/2 c are coincident with the space-group mirror plane while the mirror planes of the other molecules are inclined at slightly more than 45° to the space-group mirror plane.

Welberry considers the room temperature form of acenaphthylene to have the same general packing arrangement as the low temperature form. The absence of any high order reflections is considered to indicate a large amount of thermal motion even to the extent that the acenaphthylene molecules might be free to rotate in their own planes. As a consequence of this disorder any structure assigned to the room temperature form would only be an approximate one since the molecular orientations at any given site would be constantly changing.

The effect of pressure on acenaphthylene has been investigated using Bridgman anvils taken to an average pressure of 50 kilobars and using the large volume high pressure apparatus at pressures of 90 kilobars and 250 kilobars. The work at 50 kilobars partially duplicates an investigation by Bradbury et al. (*19*) on acenaphthylene. When using the Bridgman anvils, the sample was placed between two sheets of aluminum foil and then inserted between the 3/8 in. diameter flats of the two opposed Bridgman anvils. Unfortunately, large pressure gradients develop across the flats of this apparatus and usually the sample material which is located near the center of the flats has a considerably different appearance from that which is located near the circumference indicating a nonuniform pressure across the flat. Also, the samples of the Bridgman anvil apparatus are subjected to considerably more shear than the samples of the supported taper high



la

FIG. 1a. Infrared spectra of acenaphthalene and of polyacenaphthalene produced thermally at one atmosphere.

pressure apparatus. The extent and importance of shear in the reactivity of compounds is yet to be determined.

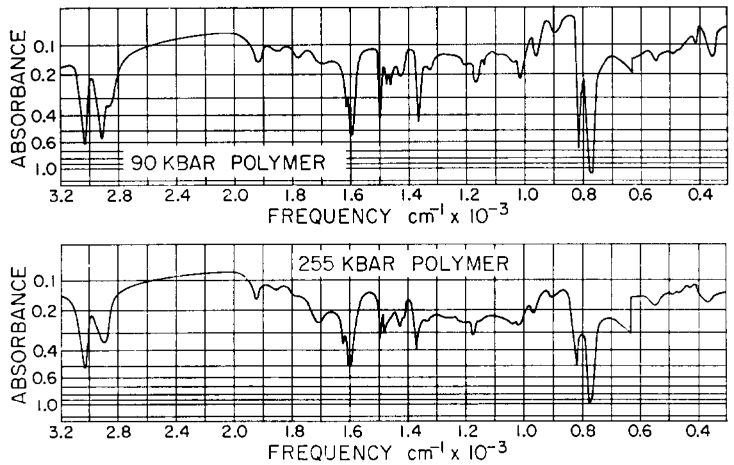
The infrared spectrum of acenaphthylene is shown in Fig. 1a. The peak at 3050 wave numbers is actually split into two peaks, one at 3060 wave numbers corresponding to olefinic carbon-hydrogen stretching vibrations at the 1 and 2 carbons and a second peak at 3040 wave numbers corresponding to aromatic carbon-hydrogen stretching vibrations at the other 6 carbons. These assignments are based upon the location of the aromatic peak in acenaphthene (3040 wave numbers). The peaks at 830, 770, and 725 wave numbers are thought to be due to carbon-hydrogen out of plane bending vibrations with the peak at 725 wave numbers probably being due to the hydrogens attached to the 1 and 2 carbons. The peaks between 1500 and 1000 wave numbers are due primarily to skeletal vibrations and have not been assigned.

In Fig. 1a is also shown the infrared spectrum of polyacenaphthylene which was formed from acenaphthylene heated to 110°C. There is a single peak at 3040 wave numbers due to the aromatic carbon-hydrogen stretching vibrations instead of the two peaks found in acenaphthylene. The peak at 2910 wave numbers is due to the saturated carbon-hydrogen stretching vibrations associated with the locations that would be the 1 and 2 carbons of acenaphthylene but which are part of the polymer chain in polyacenaphthylene. The three peaks near 1600 wave numbers appear at exactly the same energies in the spectrum of acenaphthene. The two peaks at 1495 and 1370 wave numbers appear to correspond to similar peaks in the acenaphthylene spectrum. The peaks at 830 and 770 wave numbers are due to the same carbon-hydrogen out-of-plane bending vibrations found in acenaphthylene.

When acenaphthylene was subjected to 50 kilobars at 25°C for 30 hr using Bridgman anvils, it reacted to form an off-white product in 30% yield which was insoluble in 95% ethanol but completely soluble in benzene. Comparison of its infrared spectrum with that of polyacenaphthylene indicates that the two spectra are nearly identical except for the appearance in the 50 kilobar product of a small broad peak located at roughly 1720 wave numbers which does not even appear to be faintly present in the spectrum of polyacenaphthylene.

Subjecting acenaphthylene to 90 kilobars in the large volume high pressure apparatus produced results similar to those at 50 kilobars. A yellowish-white product was formed in about 30% yield after 24 hr at 25°C which was insoluble in 95% ethanol but completely soluble in benzene. Its infrared spectrum, shown in Fig. 1b, is nearly identical to that of polyacenaphthylene and the 50 kilobar product except that the peak due to the saturated carbon-hydrogen stretching vibrations at 2910 wave numbers appears to be considerably more intense than in either the 50 kilobar product or polyacenaphthylene, the peak at 1720 wave numbers which does not appear in polyacenaphthylene is less than the same peak appearing in the 50 kilobar product, and a very small peak appears at 1480 wave numbers which is in neither polyacenaphthylene nor in the 50 kilobar product.

Acenaphthylene held at 255 kilobars and 25°C for



1b

FIG. 1b. Infrared spectra of 90 kbar and of 255 kbar polyacenaphthalene.

24 hr reacted to form a product which was brownish-red in color. The yields were a 4% product which was insoluble in 95% ethanol but soluble in benzene and an 80% product which was insoluble in 95% ethanol, benzene, and boiling zylene. Since the infrared spectra of the soluble and insoluble products were identical for all practical purposes, only the infrared spectrum of the insoluble product appears in Fig. 1b. When this spectrum is compared with that of the 90 kilobar product, the most noteworthy differences are that the peaks are much broader for the material formed at 255 kilobars and that the broad peak at 1720 wave numbers which is barely visible in the spectrum of the 90 kilobar product is quite prominent in the 255 kilobar product. Unfortunately, the peak at 1720 wave numbers cannot be assigned to any vibrational mode at present.

If polyacenaphthylene which has been produced thermally is placed under a pressure of 90 kilobars at 25°C for 24 hr, the material recovered is in the form of a yellow, translucent, almost transparent, disc. Analysis of this material indicates that it is unchanged from the starting material. If, however, polyacenaphthylene is taken to a pressure of 255 kilobars at 25°C for 24 hr, the material recovered is in the form of a bright red, almost ruby, colored disc which is nearly transparent. Analysis of this product indicates that essentially all of the material recovered is insoluble in boiling benzene and yields an infrared spectrum which is essentially identical to that of the product obtained from acenaphthylene when reacted at 255 kilobars and 25°C.

The electronic spectra for acenaphthylene, the 90 kilobar polymer, and the 255 kilobar product, all in the solid state, in KBr, are shown in Fig. 2. The spectrum of the 255 kilobar product was determined using a sample concentration that was 4 times the concentration used in determining the spectrum ot the 90 kilobar polymer. It appears that the locations of the peaks are essentially the same in both the 255 and 90 kilobar products but the intensities are considerably lower in the 255 kilobar product than in the low pressure product. Neither the 90 kilobar nor the 255 kilobar product shows the two peaks at

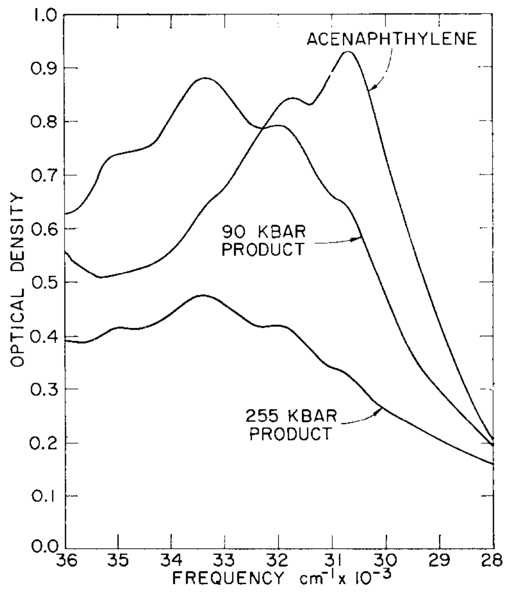


FIG. 2. Electronic spectra of acenaphthalene, 90 kbar polymer and of 255 kbar polymer at one atmosphere.

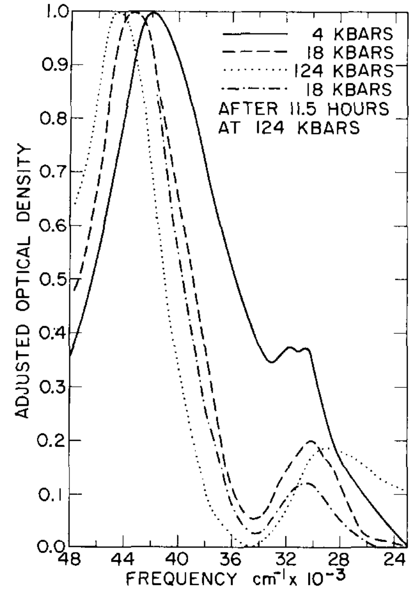


FIG. 3. Electronic spectra of acenaphthalene as a function of pressure.

TABLE II

SHIFT OF OPTICAL ABSORPTION PEAKS WITH PRESSURE FOR ACENAPHTHALENE AND POLYACENAPHTHALENE

Pressure (kbar)	Peak I	Peak II
	A. Acenaphthalene	
4	42 000 cm^{-1}	30 600 cm^{-1}
18	43 500 cm^{-1}	30 100 cm^{-1}
46	44 200 cm^{-1}	29 500 cm^{-1}
75	44 300 cm^{-1}	29 000 cm^{-1}
101	44 300 cm^{-1}	28 800 cm^{-1}
124	44 600 cm^{-1}	28 800 cm^{-1}
	B. Polyacenaphthalene	
10	42 000 cm^{-1}	31 600 cm^{-1}
20	42 500 cm^{-1}	31 300 cm^{-1}
49	43 500 cm^{-1}	30 400 cm^{-1}
75	44 400 cm^{-1}	30 100 cm^{-1}
100	44 500 cm^{-1}	30 000 cm^{-1}
121	44 600 cm^{-1}	29 400 cm^{-1}
140	44 800 cm^{-1}	28 900 cm^{-1}

386 and 407 nanometers which have been reported to be present in the spectrum of polyacenaphthylene produced radiochemically (*18*).

In Fig. 3 are shown the electronic spectra of acenaphthylene obtained using the high pressure optical apparatus. Michl and Zahradnik (*21*) have discussed the electronic spectrum of acenaphthylene using the LCMO theory and concluded that the transitions cannot be assigned labels consistent with those proposed by Klevens and Platt (*22*) for cata-condensed hydrocarbons. The most noteworthy features of the high pressure electronic spectra are the shift of the high energy peak at 42 000 cm^{-1} to still higher energy reaching an energy of 44 600 cm^{-1} at 124 kilobars and the shift of the low energy peak at 30 600 cm^{-1} to lower energy with the elimination of vibrational structure and the gradual broadening of the peaks leading to an extensive tail at 124 kilobars that reaches quite some distance out into the visible region. When the pressure on the sample is reduced to 18 kilobars after having been at 124 kilobars for 11.5 hr, the high energy peak returns to the same location (43 500 cm^{-1}) that it occupied at 18 kilobars previous to having been subjected to 124 kilobars. After 11.5 hr at 124 kilobars the low energy peak at 30 500 cm^{-1} in the 18 kilobar spectrum appears to have shifted slightly to lower energy and to have lost intensity relative to the 43 500 cm^{-1} peak when compared with the original 18 kilobar spectrum. The peak locations are given in Table II.

The high pressure electronic spectra of polyacenaphthylene produced thermally are shown in Fig. 4. The spectrum of polyacenaphthylene is similar to that of acenaphthene and may be considered as a disubstituted naphthalene. On this basis the peak at 31 600 cm^{-1} is due to the $^1L_a \leftarrow {}^1A$ transition while the peak at 42 000 cm^{-1} is due to the $^1B_b \leftarrow {}^1A$ transition following the nomenclature of Klevens and Platt (*22*). The peak at 31 600 cm^{-1}

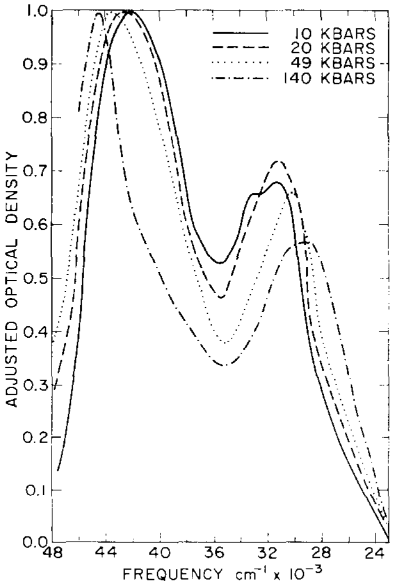


FIG. 4. Electronic spectra of polyacenaphthalene as a function of pressure.

shows considerable vibrational structure in solution and somewhat less in the solid state at atmospheric pressure. At a pressure of 10 kilobars most of this structure has disappeared and at higher pressures any vibrational structure which might be present cannot be detected by the spectrophotometer. A very weak peak occurs in the solution spectrum of polyacenaphthylene at about 31 000 cm^{-1} which is presumed to be due to the $^1L_b \leftarrow {}^1A$ transition. This peak is barely detectable in the solid state spectrum of polyacenaphthylene and is not detectable at all by the high pressure spectrophotometer.

The application of pressure to polyacenaphthylene produces results similar to those for acenaphthylene. The high energy peak shifts blue (to higher energy) with increasing pressure while the low energy peak shifts red. The low energy peak loses intensity relative to the high energy peak with increasing pressure but does not develop the extensive tail at high pressures which is so apparent in acenaphthylene. When polyacenaphthylene is subjected to 140 kilobars for several hours the spectra show no hysteresis related to pressure. In other words, the spectrum obtained for polyacenaphthylene at 20 kilobars with no high pressure history is identical to the 20 kilobar spectrum of a sample which has previously been held at 140 kilobars for an hour. The peak locations appear in Table II.

X-Ray powder photographs were taken of the high pressure products. Whereas the powder photograph of acenaphythylene has many well defined lines, polyacenaphthylene produced thermally has 3 or 4 extremely diffuse lines which are barely detectable, indicating that the thermal polymer is not crystalline. When samples from high pressure runs were taken directly and X-rayed without any purification, the only lines visible were diffuse ones which were attributable to the acenaphthylene diffraction pattern. After removal of the unreacted acenaphthylene from the 90 kilobar product the powder pattern resembled that of the thermal polyacenaphthylene. The powder pattern of the portion of the 255 kilobar product which was insoluble in benzene did not exhibit any detectable lines, so it must exist in an extremely disordered form in the solid state.

In the characterization of the high pressure products of acenaphthylene it would have been useful to know the molecular weights. Polyacenaphthylene formed at 100°C in the melt is reported to have molecular weights on the order of 3500 (*9*) while polyacenaphthylene formed in solution using BF_3 as an initiator has molecular weights in the range of 150 000 (*10*). Unfortunately, the present methods for determining the molecular weights of high polymers require that the material be soluble (which eliminated the 255 kilobar insoluble product) and that a fairly large amount of material be available, as the present micro methods for determining molecular weights are largely limited to low molecular weight materials (*23*).

Several experiments were performed to determine the effect of very low temperatures upon the reactivity of acenaphthylene. The effect of temperature was considered to be important in light of the ordering of the crystal structure below −130°C. When acenaphthylene was taken to a modest pressure, cooled to liquid nitrogen temperature, and then subjected to 90 kilobars for 6.5 hr at liquid nitrogen temperature, the acenaphthylene failed to react to any detectable extent. In another experiment, acenaphthylene was subjected to a modest pressure, cooled to liquid nitrogen temperature, and then taken to 90 kilobars. After reaching 90 kilobars the sample was allowed to warm slowly to 25°C and then stand for 24 hr. At the end of this time the sample was again cooled to liquid nitrogen temperature and the pressure removed. The recovered sample was brownish-yellow and analysis indicated that it was 29% soluble polymer and 3% insoluble polymer. The infrared spectra of the soluble and insoluble portions were both identical to that of the 90 kilobar product produced at 25°C.

For the sake of completeness, several experiments were run using diacenaphthylene and acenaphthene to determine the behavior of these compounds at very high pressures. Since diacenaphthylene decomposes at 200°C to form acenaphthylene, it appeared that it might possibly decompose under pressure to form either acenaphthylene or a polymer; however, when it was subjected to 255 kilobars at 25°C for 24 hr there was no detectable change in the material. Acenaphthene also failed to react to any detectable extent at 255 kilobars and 25°C after 24 hr. The product yields for a number of high pressure experiments are summarized in Table III.

Yamada, Yanagita, and Kobayashi (*24*) have dealt with the possible conformations in which polyacenaphthylene might be found. While we cannot characterize the polymer mode at 90 kilobar effectively, the similarity of its infrared spectrum to that of thermal polyacenaphthalene would indicate that its structure is probably similar. The fact that the same insoluble product can be made at 255 kilobars starting either from acenaphthalene or from the thermal polymer is further evidence that the 90 kilobar product is very similar to the thermal product.

TABLE III

POLYMER YIELDS UNDER HIGH PRESSURE FOR ACENAPHTHYLENE AND RELATED COMPOUNDS

	Soluble polymer	Insoluble polymer
Acenaphthylene 50 kilobars, 25°C, 30 hours	30%	0%
Acenaphthylene 90 kilobars, 25°C, 1 minute	15	0
Acenaphthylene 90 kilobars, 25°C, 10 minutes	18	0
Acenaphthylene 90 kilobars, 25°C, 24 hours	30	4
Acenaphthylene 255 kilobars, 25°C, 24 hours	4	80
Polyacenaphthylene 90 kilobars, 25°C, 24 hours	100	
Polyacenaphthylene 255 kilobars, 25°C, 24 hours		100
Diacenaphthylene 90 kilobars, 25°C, 24 hours	0	0
Diacenaphthylene 255 kilobars, 25°C, 24 hours	0	0
Acenaphthene 255 kilobars, 25°C, 24 hours	0	0
Acenaphthylene 90 kilobars, −195°C, 24 hours	0	0

The reactions which acenaphthylene and polyacenaphthylene undergo at 255 kilobars and room temperature are difficult to elucidate. Both materials react to form what appears to be the same product, a red, insoluble, noncrystalline solid which sometimes is almost transparent. The major difference between its infrared spectrum and that of polyacenaphthylene is that its spectrum contains an additional broad peak at approximately 1720 wave numbers and that all the peaks in its spectrum are broader than those in polyacenaphthylene. What the broad peak at 1720 wave numbers represents cannot be determined at present. The broadening of the peaks and the decline in solubility indicate a more complicated polymer than polyacenaphthylene, but whether this change is due to intra-polymer or inter-polymer bonding is very difficult to establish.

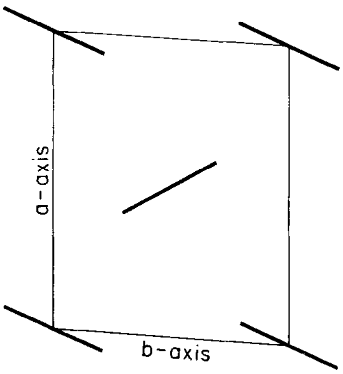
Pentacene

The earlier work on pentacene (*1*) in which the irreversible behavior was discovered, yielded only enough sample for an electronic spectrum. It was speculated that dipentacene was formed, by anology to the photodimer of anthracene, and the similar product alleged for pentacene (*25*). It would appear that this latter product is not formed photochemically (*26*). In the present study we show that the photodimer is not formed at high pressure, but probably a polymer, with a different structure.

The crystal structure of pentacene has been determined by Campbell, Robertson, and Trotter (*27*) and later revised (*28*). Pentacene is triclinic with $a = 7.90$ Å, $b = 6.06$ Å, $c = 16.01$ Å, $\alpha = 101.9°$, $\beta = 112.6°$, $\gamma = 85.8°$, $D_{\text{calcd}} = 1.33$ grams per cubic centimeter, and $D_{\text{meas}} = 1.32$ grams per cubic centimeter. Figure 5 shows the approximate orientation of the intersections of the molecular planes with the *a–b* plane.

In Fig. 6 are shown the infrared spectra of pentacene and of the product which has been subjected to 350 kilobars for 24 hr at 25°C. No purification was attempted on the recovered sample.

In the infrared spectrum of pentacene a few of the peaks can be assigned with some degree of confidence. The peak at 3030 wave numbers corresponds to the aromatic carbon-hydrogen stretching frequency. The peak at 470 wave numbers resembles a similar peak in naphthalene which has been assigned to an out-of-plane skeletal bending mode. The peaks at 725, 830, and 900 wave numbers are probably due to carbon-hydrogen out of plane bending vibrations. Most of the peaks between 2000 and 1000 wave numbers are due to a number of different skeletal vibrations. Inspection of the high pressure reaction product spectrum shows that many of the peaks present in the pentacene spectrum have disappeared while others have broadened to a considerable extent. A new peak has appeared at 2900 wave



Scale : 1 cm = 1 Å

FIG. 5. a-b Plane of pentacene crystal.

numbers which is due to saturated carbon-hydrogen stretching vibrations. There are also broad peaks at 1670, 1600, 1450, 1275, 1175, 1075, 800, 515, 395, and 370 wave numbers which do not appear in the spectrum of pentacene. The extremely broad peak at 1075 wave numbers might appear to be due to pyrophyllite contamination, as it is a peak near this location. However, other peaks in the pyrophyllite spectrum do not appear. Pyrophyllite contamination is therefore considered to be negligible.

There are some similarities between the infrared spectra of the reaction product and of pentacene peroxide produced photochemically, in that both have peaks at or near 3030, 2905, 1670, 1495, 1450, and 1390 cm^{-1}. However, the relative intensity of peak representing the saturated C–H stretch is significantly greater in the high pressure material, and the peaks are much broader generally. The peroxide is much more soluble in all solvents than the high pressure product. In any case, there can be no significant amount of oxygen in the reaction mixture, so the peroxide can be eliminated as the high pressure product.

The electronic spectra of pentacene and of the high pressure product appear in Fig. 15 of Ref. (*1*). The low energy peaks on the spectrum of pentacene have apparently disappeared as one would expect if electrons were no longer conjugated around the entire perimeter. The spectrum of the high pressure product is probably a mixture of scattering and a variety of $\pi^* \leftarrow \pi$ transitions from various residual structures of benzene, naphthalene, anthracene and tetracene found in the product.

Powder X-ray photographs were obtained for both the high pressure reaction product and for pentacene. The unpurified high pressure material exhibited four very weak lines which were found to correspond to the four strongest lines in the pentacene powder photograph. It seems probable that unreacted pentacene is responsible for these lines, and the high pressure product is amorphous.

Although reactions in the solid state are thought to proceed as a result of the migration of lattice imperfections (*29*), it seems most probable that the configuration in which pentacene reacts at very high pressures will be a deformation or a modification of the crystal structure at one atmosphere. Looking at the intersections of the pentacene molecular planes with the *a*–*b* plane in Fig. 6, it is reasonable to expect that the *a* axis and the *b* axis would be compressed with increasing pressure. Shortening the *b* axis would develop interactions between location 4 of one pentacene molecule and location 1 of the next molecule along the *b* axis. Similar interactions will develop between location 5 of molecule one and locations 1 and 14 of the next molecule. Also interacting will be location 6 of molecule one with 13 and 14 of the next molecule, location 7 of molecule one with 12 and 13 of the next molecule, and location 8 of molecule one with 11 and 12 of the next molecule. If the two molecules are forced close enough together, the π orbitals of the two molecules might overlap sufficiently to allow polymerization to take place along the *b* axis in a manner as illustrated in Fig. 7a. The reactive sites would not necessarily be 6 and 13 although the reactivity of the 9 and 10 locations in anthracene might seem to indicate this. Actually, the reactivity of these locations in anthracene only indicates that the inner rings of a polyacene have sites which are more reactive than those of the

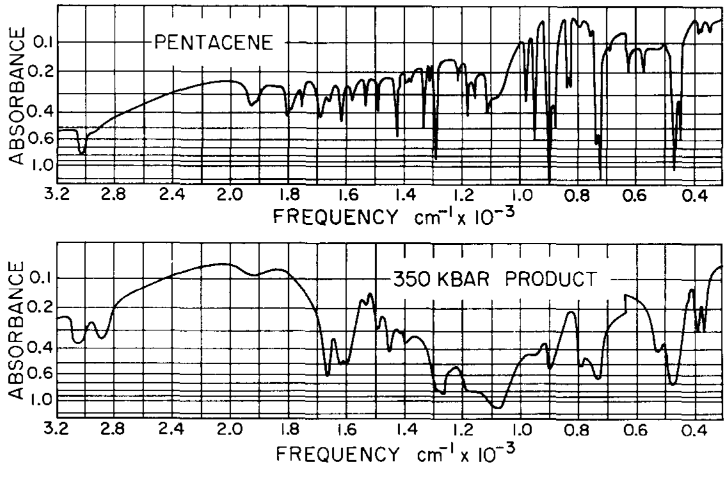
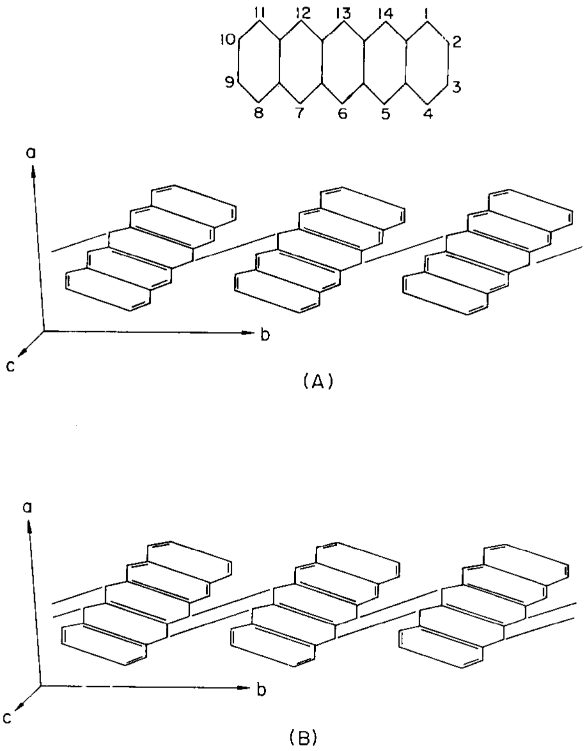


FIG. 6. Infrared spectra of pentacene and 350 kbar product.



(A)

(B)

FIG. 7. Possible trans polymerizations of pentacene along the b axis.

two end rings. One can say little about the reactivity in pentacene of the sites 7 and 12 compared with 6 and 13 based upon the reactivity of anthracene. The reaction need not be limited to one intermolecular bond between pentacene molecules along the chain but might involve two or three, forming a wrinkled sheet as shown in Fig. 7b. This would be consistent with the apparent fraction of aliphatic C–H bonds.

The polymerization need not be regular. In other words, the chain might propagate from location 6 to location 14 on the next molecule and then it might propagate from location 5 to either location 1 or location 14 of the next molecule. The above illustrated polymerizations would all be trans additions. Such addition would require that the mers of the polymer be nearly planar in order for them not to collide. The more intermolecular bonds formed, however, the easier this would be. Also, these polymers would be expected to be noncrystalline since the molecular planes of the mers do not correspond to the plane in which the polymer would propagate.

Another possibility is a polymerization which would involve cis additions. This might result from the interaction of the two layers of pentacene molecules at 0 and 1/2 a with propagation in the *b* direction. It would require some major reorientations of the pentacene molecules, but such drastic changes might result from high pressure and shear. Such a polymer would appear as shown in Fig. 8. The pentacene mers in such a polymer would undoubtedly not be planar but bent as the anthracene mers are in dianthracene. Assuming this to be true, the polymer would probably be noncrystalline. The cis form must be considered a less likely product than the trans form due to the extensive amount of rearrangement required for polymerization.

In either cis or trans addition, an increase in the number of linkages between pentacene mers would generate a material which could be considered an intermediate form in the eventual development of a

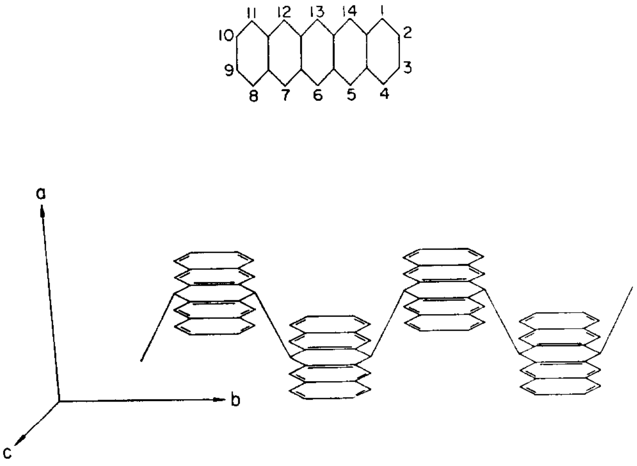


FIG. 8. Possible cis polymerizations of pentacene.

structure with sheets of carbon such as found in graphite. This, of course, would require the evolution of hydrogen. Although this has not been observed for pentacene, a number of other organic materials have been observed to "blow out" at high pressures upon several occasions in this laboratory. It is possible that the "blow out" is caused by gas escaping from the cell, however, the exact nature of the material evolved has not yet been determined due to the difficulties of reproducing this phenomenon and the difficulty of collecting a sample of the material which has escaped from the cell. The material remaining in the cell under such circumstances is a black, amorphous powder which has an infrared spectrum showing absolutely no detail.

It is of interest to discuss the mechanism of reactivity of polyacenes in the solid state under very high pressures. From the work of this paper and others (*1*, *2*) it appears that the reactivity of the polyacenes under pressure increases with the number of rings. Hexacene and pentacene have both been observed to react under very high pressures while naphthalene, anthracene, and tetracene have not yet been observed to react to any detectable extent. Since all of these compounds have very similar crystal structures (*25*, *27*, *28*, *30*, *31*), it is quite unlikely that the differences in reactivity are due to the topochemistry of the system as it appears to be in the photochemical dimerization of transcinnamic acid (*32*).

The reactivity of the polyacenes under pressure appears to be related to the energies of their low lying unoccupied energy levels. The energy levels of the polyacenes have been identified by Klevens and Platt (*22*) and their nomenclature will be used throughout this discussion. The three observed lowest lying states of the polyacenes are the ^3L_a, ^1L_b, and ^1L_a. The values of these energy levels (for the polyacene dissolved in benzene) as given by Klevens and Platt (*22*) and Lewis and Kasha (*33*) are listed in Table IV. The ^3L_a states for tetracene and pentacene have not been observed experimentally. If these triplet states do exist, they would be expected to be of very low energy and of very low intensity making it very difficult to observe them. Table IV indicates that as the number of rings increases in the polyacene series, the energy of the lowest levels decreases. In benzene and naphthalene the lowest singlet state is ^1L_b whereas in the polyacenes with three or more rings the lowest singlet state is ^1L_a.

The relationship of the reactivity of polyacenes at high pressure and their electronic spectra may be explained by a combination of two phenomena. The first of these is that a new reactive ground state may form at high pressures by mixing the original atmospheric ground state with one of the lower lying unoccupied energy levels that has been lowered (relative to the ground state) by the increased pressure. The second is that a new reactive ground state may be created under pressure by forcing the molecules into such close proximity that they form self complexes.

TABLE IV

POLYACENE ENERGY LEVELS (IN k wave NUMBERS)

	^3L_a	^1L_b	^1L_a
Benzene	29.8	38.0	48.05
Naphthalene	21.3	32.0	34.6
Anthracene	14.7	28.5(?)	26.4
Tetracene	?[a]	25.5(?)	21.1
Pentacene	?[a]	24.0	17.1

[a] The two ^1L_b values followed by (?) are in doubt due to the presence of vibrational structure from another peak.

The electronic spectra of anthracene (*34*, *35*), tetracene (*1*, *35*), and pentacene (*1*, *35*) have been studied at high pressures. The lowest lying peak (which corresponds to transitions from the ground state to the ^1L_a state) shifts to lower energy with increasing pressure in all three of these, the shift being approximately 5500 wave numbers in the first 55 kilobars for each one. In other words, at this pressure the ^1L_a state is 10 900 cm^{-1} above the ground state in pentacene, but considerably higher for anthracene and tetracene. The red shift continues to higher pressure, but at a reduced rate. It is thus entirely possible that pressures on the order of 200 kilobars would be expected to lower it to such an extent that it could be populated thermally. To achieve a similar situation in tetracene or anthracene would require much higher pressures. The situation, therefore, appears to be that of Fig. 9 which shows schematic potential energy diagrams for pentacene and anthracene, the abscissa being some generalized coordinate characteristic of the molecule. In anthracene the ^1L_a state is lowered to ^1A but not sufficiently to develop any interaction between the two states. The ^1L_a state in pentacene, however, is low enough initially and shifts to lower energy with pressure to such an extent that the ^1L_a state becomes significantly populated due to thermal excitation of electrons from the ^1A state. The ground state,

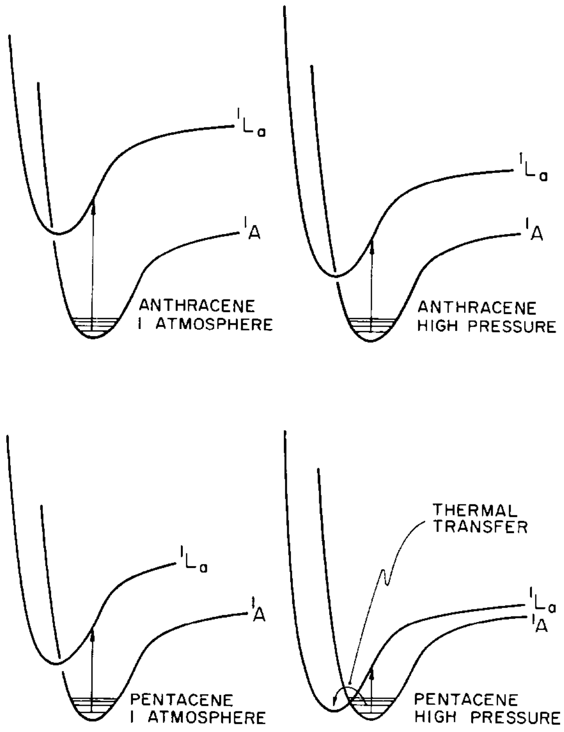


FIG. 9. Schematic potential energy diagrams for anthracene and pentacene.

therefore, is no longer strictly ^1A but rather is defined by

$$\psi_{gs} = a\psi(^1A) + b\psi(^1L_a) + \cdots,$$

where ψ_{gs} is the wave function of the ground state, $\psi(^1A)$ is the wave function of the 1 atmosphere ground state ^1A, $\psi(^1L_a)$ is the wave function of the ^1L_a state, and $+\cdots$ represents negligible contributions. At 1 atmosphere $a \gg b$ and the second term is negligible, while at high pressures b is large enough to make a significant contribution. With this contribution the ground state would begin to assume some of the characteristics of the ^1L_a state, such as its polarization (see Fig. 3 of Ref. (*36*)). This would appear to enhance the probability of polymerization by trans addition as described previously.

The second possibility, that of the pentacene molecules forming a new, reactive ground state at high pressures due to self-complexing, is based upon the treatments by Mulliken (*37*) and McGlynn (*38*) of the theoretical self-complexing of benzene. Although a benzene self-complex has never been observed, the crystal structures of many multiring aromatic compounds appear at least to be partially determined self-complexing. Both of the above treatments for benzene are for (1 : 1) self complexes. It is unlikely that pentacene would form a (1 : 1) complex; it is more likely that it would form an *n*-component self-complex which would have the following ground state

$$\begin{aligned}\psi_{gs} = a^1\,\psi_0(P_1 P_2 \cdots P_k \cdots P_{n-1} P_n) \\ + \frac{b}{\sqrt{2}}\Big[{}^1\psi_1(P_1{}^+ P_2{}^- \cdots P_k{}^+ \cdots P_{n-1}^{+} P_n{}^-) \\ + {}^1\psi_2(P_1{}^- P_2{}^+ \cdots P_k{}^- \cdots P_{n-1}^{+} P_n{}^+)\Big].\end{aligned}$$

At one atmosphere $a \gg b$ but at high pressures b would become significantly larger. There is no experimental data available to indicate what orientation the pentacene molecules would be expected to assume if self-complexing developed. Based upon the treatment of the (1 : 1) benzene complex the situation in which the pentacene molecules are superposed one above the other with their axes coincident can be eliminated. The most likely orientations would be those in which the pentacene molecules lie in parallel planes and the longitudinal and transverse axes are parallel but displaced from coincidence, or those in which the molecules are coplanar and lying side by side. Either one of these might be evolved from the one atmosphere crystal structure of pentacene. Such redistribution of charge as found in a self-complex may promote the propagation of a polymerization reaction.

The reactivity of pentacene due to a change in ground state is similar to the reduction of ferric ion at high pressure (*39*, *40*) and the change in the spin state of iron at high pressure (*40*). Ferric ion reduces to ferrous ion at high pressures due to the transfer of an electron from a predominantly ligand orbital to a predominantly metal orbital creating a ground state that consists of a ferrous ion plus a free radical associated with the ligands. When the spin state increases under pressure, the new ground state is usually regarded as a state in which the ligand orbitals are primarily occupied by ligand electrons and the metal electrons are relocalized on the iron, giving rise to a higher spin configuration.

The failure of pentacene to react at temperatures below 180°K is assumed to be due to the curtailment of certain molecular motions in the lattice associated with temperatures above 180°K. These movements might affect molecular orientations adequately to determine whether intermolecular bonding would develop or not. The molecular motions in crystalline pentacene may, in a restricted sense, be similar to the in-plane rotations of acenaphthylene at temperatures above 150°K. The crystal structure of pentacene, however, would restrict such vibrations to things like slight changes in the inclination of the molecular plane relative to the crystallographic axes or distortion of the molecular plane.

TCNE—Hydrocarbon Complexes and Related Compounds

Bentley (*2*) studied tetracyanoethylene complexes at very high pressure using the electrical resistance apparatus developed in this laboratory. He found irreversible behavior in the (1:1) complexes with perylene, naphthalene, and azulene. It was speculated on very limited evidence that TCNE-naphthalene formed a Diels-Alder adduct similar to the one formed by TCNE and anthracene at 25°C and one atmosphere in solution.

Here we report high pressure results on TCNE-naphthalene and TCNE-perylene complexes and on the TCNE-anthracene Diels-Alder adduct.

The crystal structure of TCNE-perylene has been determined by Ikemoto, Yakushi, and Kuroda (*41*) and found to be similar to that of TCNE-pyrene (*42*). The crystal structure of the TCNE-naphthalene (1 : 1) complex has been determined by Williams and Wallwork (*43*) and the structure of the TCNE-anthracene Diels-Alder adduct has been determined by Karle and Fratini (*44*).

In Fig. 10 is shown the infrared spectra of the TCNE-perylene complex and the high pressure product formed at 90 kilobars and 25°C. In the spectrum of the complex the peak at 3050 wave numbers is due to aromatic carbon-hydrogen stretching vibrations and the two peaks at 2260 and 2220 wave numbers are due to CN stretching vibrations. The remainder of the spectrum consists primarily of peaks which appear in either the spectrum of TCNE or that of perylene and of a few peaks which are characteristic of the complex. The spectrum of the 90 kilobar product is particularly remarkable for its almost complete lack of detail. There is a small peak at 3040 wave numbers due to aromatic carbon-hydrogen stretching vibrations, an extremely weak peak at 2910 wave numbers due to saturated carbon-hydrogen stretching vibrations, a strong peak at 2210 wave numbers due to CN stretching vibrations, an extremely broad peak centered around 1580 wave numbers with general adsorption between 1450 and 950 wave numbers, and a peak at 765 wave numbers due probably to some type of carbon-hydrogen bending vibration. It is fairly obvious that the product formed at 90 kilobars and 25°C is a polymer which is quite complex. It is definitely not a Diels–Alder adduct. The spectra of products formed at other pressures are similar to that of the 90 kilobar product.

The spectrum of the high pressure product obtained from the TCNE-naphthalene complex was similar in almost all features to that of the TCNE-perylene product, with only some minor differences in peak intensities.

When the Diels–Alder adduct of TCNE with anthracene was compressed to 225 kilobars, a product was produced with an infrared spectrum very similar to that obtained from the high pressure products from the complexes, and entirely different from the adduct. Apparently, the latter is destroyed and a relatively complex polymer is formed.

The electronic spectra of the high pressure products were substantially featureless. In particular, the charge transfer peak has disappeared.

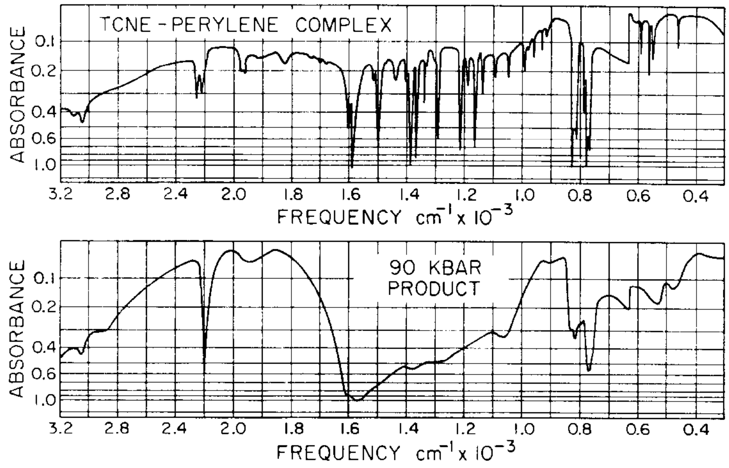


FIG. 10. Infrared spectra of TCNE-perylene complex and 90 kbar product.

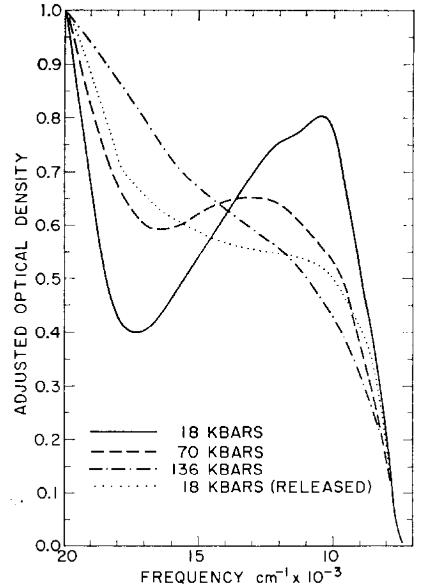


FIG. 11. Electronic spectra of TCNE-perylene complex as a function of pressure.

In Fig. 11 is shown the electronic spectra of the TCNE-perylene complex as a function of pressure to 140 kilobars. The most striking feature is the irreversible fading of the charge transfer peak, which would be expected in view of the reactivity.

Two Russian investigators, Berlin and Matveyeva (*45*), have studied the copolymerization of TCNE with anthracene and found that at 200°C in sealed evacuated ampoules TCNE polymerizes with anthracene at a mole ratio of 4:1. The infrared spectrum of the product obtained under the conditions described by them is nearly identical to that obtained for the products made at high pressures except that the thermal polymer appears to have little if any absorption associated with the carbon-hydrogen stretching vibrations. Whether or not the porphyrin rings which Berlin and Matveyeva describe would be formed under pressure could not be determined.

Acknowledgment

The authors wish to thank Mr. Richard Welberry and Professor Judith Milledge for making available to us Mr. Welberry's unpublished analysis of the crystal structure of acenaphthalene. It has been most helpful.

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