Some most interesting examples of oxidative addition of silicon hydrides to complexes of Mn and W have been recently described by Hart-Davis and Graham.[11,12] One of these reactions exhibited many features in common with those presently described.[11] More interesting perhaps was the observation that the hydride ligand in π-$(C_5H_5)Mn(CO)_2(Ph_3Si)H$, while being located at a "normal" distance from the Mn, was also "close enough to silicon to imply some degree of bonding."[13] It is quite possible that this compound represents a case where the descent to the energy minimum of idealized seven-coordinated Mn(III) is arrested, probably by steric repulsion, before complete separation of the Si–H bond. The possibility that the close Si–H distance is due to steric constraints has also been raised by Bennett and Simpson.[13]

Although a kinetic study of hydrogen addition to **1** has recently been reported, the results were too incomplete to test the validity of the deformation hypothesis for that system.[14] There does not seem to be any reason why good activation parameters for the hydrogen reaction cannot be obtained and our prediction that the ratio of rate constants for hydrogen addition and phosphine addition to **2** be independent of temperature put to the test.

Experimental Section

All the silicon hydrides used were purchased from PCR, Inc.

Triethoxysilane and diethoxymethylsilane were purified by distillation, and trimethylsilane was used without purification.

Hydridocarbonyltris(triphenylphosphine)iridium(I) was prepared according to the procedure of Yagupsky and Wilkinson.[15]

All solvents were dried by distillation from calcium hydride and saturated with nitrogen prior to use.

Kinetic Measurements. Rate measurements were made by following the disappearance of the 323 mμ peak of the iridium(I) complex. A Hitachi-Perkin-Elmer Model 124 spectrometer from Coleman Instruments, equipped with a Haake Model KT 41 temperature controller, was used for the spectroscopic measurements. The reactions were run under pseudo-zero-order conditions with respect to silicon hydrides and triphenylphosphine.

Equilibrium constants were measured under the conditions at which both iridium(I) and iridium(III) complexes existed, using Job's method.

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[11] A. J. Hart-Davis and W. A. G. Graham, *J. Amer. Chem. Soc.*, **93**, 4388 (1971).

[12] J. K. Hoyano and W. A. G. Graham, *ibid.*, submitted for publication.

[13] M. J. Bennett and K. A. Simpson, *ibid.*, **93**, 7156 (1971).

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Reactivity of Hydrocarbon–Iodine Complexes in the Solid State at Very High Pressure[1]

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Abstract: A common effect of very high pressure is the relative shift of electronic energy levels. This shift can lead to a new ground state with different chemical and physical properties. In this paper we present the results of studies of the charge transfer complexes of I_2 with perylene and pyrene. For these systems the iodine acts as a catalyst. It provides an electronic state such that at high pressure (160–200 kbars) the hydrocarbons are placed in a reactive configuration. The products include soluble and insoluble hydrocarbon polymers. The soluble materials are fractionated into classes by chromatography, and two classes of perylene dimers and two of pyrene tetramers are reasonably characterized. Models for one of each type of compound are presented. It would appear possible to produce a variety of new products by modifications of these techniques.

In this laboratory a series of studies have been made on the effect of pressure to 500 kbars on the resistance of a variety of aromatic hydrocarbons and of their EDA complexes with a number of electron acceptors.[2–4] It was observed from the electrical resistance behavior that pentacene and hexacene undergo an irreversible transformation above 200 kbars while smaller molecules such as anthracene and tetracene apparently do not. In the original apparatus the samples were very small (~0.1 mg), but a modification with a somewhat smaller pressure range[5] permitted samples of 2–3 mg to be recovered from pressures as high as 350–400 kbars. The pentacene product exhibited the properties of a high polymer with a significant fraction of paraffinic bonding. However, its total insolubility limited the investigation to ir and electronic spectra and made any significant characterization impossible.

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

[2] G. A. Samara and H. G. Drickamer, *J. Chem. Phys.*, **37**, 474 (1962).

[3] (a) R. B. Aust, W. H. Bentley, and H. G. Drickamer, *ibid.*, **41**, 1856 (1964); (b) R. B. Aust, G. A. Samara, and H. G. Drickamer, *ibid.*, **41**, 2003 (1964).

[4] W. H. Bentley and H. G. Drickamer, *ibid.*, **42**, 1573 (1965).

[5] V. C. Bastron and H. G. Drickamer, *J. Solid State Chem.*, **3**, 550 (1971).

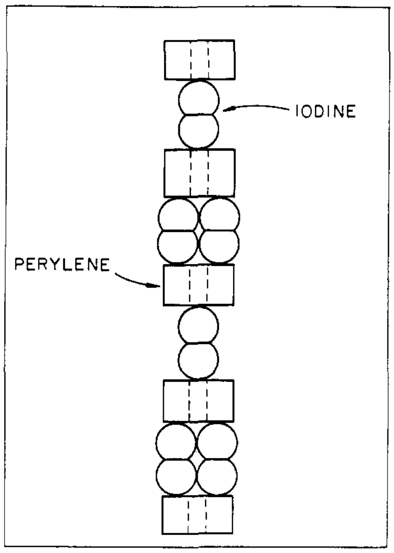

Figure 1. Probable structure of the 2 perylene·$3I_2$ complex.

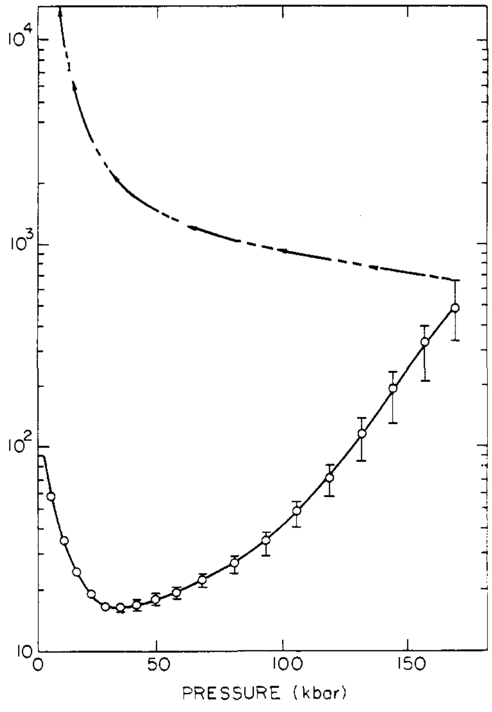

Figure 2. Resistance *vs.* pressure plot for the 2 perylene·$3I_2$ complex.

A wide variety of the electron donor–acceptor complexes studied also undergo an irreversible transition, as indicated by resistance measurements. Again, the products which have previously been examined were insoluble polymers which defied characterization.

In this paper we present the results of studies of complexes of the aromatic hydrocarbon molecules perylene ($C_{20}H_{12}$) and pyrene ($C_{16}H_{10}$) with iodine. In particular we study the 2 perylene·$3I_2$ and the pyrene·$2I_2$ complexes. A schematic representation of probable structure of the 2 perylene·$3I_2$ complex appears in Figure 1. It was developed by Uchida and Akamatu[6] from a powder X-ray pattern by analogy to the structure of the benzene-bromine complex accurately determined by Hassel and Roemming.[7] The pyrene·$2I_2$ complex can probably be assumed to have a similar layered arrangement. These complexes undergo an irreversible transformation with pressure, although the pure hydrocarbons do not, at least in the available pressure range. Resistance–pressure curves for the complexes, illustrating the irreversible behavior, are shown in Figures 2 and 3. (The vertical lines represent the drift in resistance in one minute's time.) In these cases soluble products were formed which could, in some degree, be characterized.

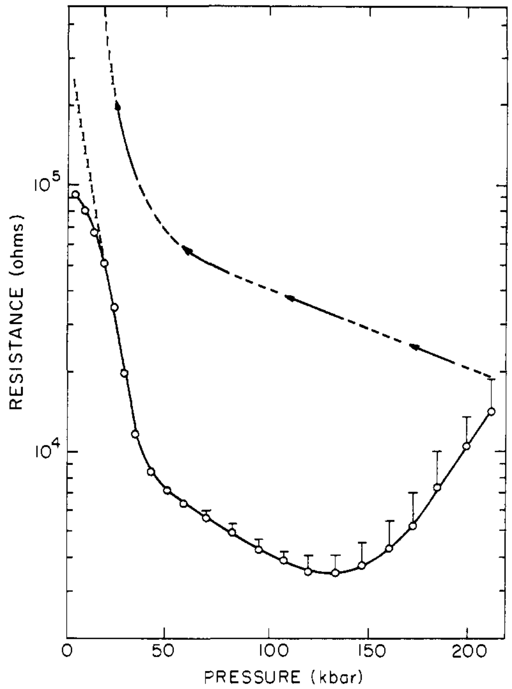

Figure 3. Resistance *vs.* pressure plot for the pyrene·$2I_2$ complex.

Before analyzing the particular reactions occurring in these compounds, it is desirable to review briefly the observed effects of pressure on electronic structure. The basic effect of compression is to increase overlap between adjacent orbitals. A consequence of this overlap is the relative displacement of one type of orbital with respect to another. If an excited state lies not too high in energy *vis-à-vis* the ground state, one may thus obtain a new ground state, or a ground state greatly modified by configuration interaction, and with very different physical and chemical properties. Such an event is called an electronic transition; it may occur continuously over a range of pressures or discontinuously at a given pressure. In general there is no change in crystal structure. The conditions for electronic transitions are discussed in detail elsewhere.[8–11] They have been observed in the heavy alkali, alkaline earth, and rare earth metals and in certain oxides where the observable consequence is a drastic change in electrical properties. In transition metal compounds, particularly those of iron, changes in the oxidation state

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(6) T. Uchida and H. Akamatu, *Bull. Chem. Soc. Jap.*, **34**, 1015 (1961)

(7) O. Hassel and C. Roemming, *Quart. Rev. Chem. Soc.*, **16**, 1 (1962).

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(10) C. W. Slichter and H. G. Drickamer, *J. Chem. Phys.*, **56**, 2142 (1972).

(11) H. G. Drickamer, C. W. Frank, and C. P. Slichter, *Proc. Nat. Acad. Sci.*, in press.

and/or the spin state of the magnetic ion are observed as a consequence of this relative displacement of orbitals.

Optical absorption is a common technique for observing differences in orbital energies. On the other hand, the high-pressure electron transfer process described as an electronic transition is a thermal process. The differences between the energies of optical and thermal processes at high pressure have been discussed in detail.[9-11] The major factors include the Franck–Condon limitation on optical processes, the selection rules for optical processes, configuration interaction which can increase the difference between the two types of processes, and the fact that different configuration coordinates may be involved in the two processes. An analysis[11] based primarily on the first factor gives the relationship (at 25°)

$$E_{\text{th}} \cong h\nu_{\max} - 3.6(\delta E_{1/2})^2 \tag{1}$$

where E_{th} is the energy of the thermal transition, $h\nu_{\max}$ is the energy of the optical peak maximum, and $\delta E_{1/2}$ is the peak half-width (all quantities in electron volts). This crude analysis has proved to be semiquantitative in predicting high-pressure electronic transitions in compounds of iron.[11]

The hydrocarbons which react at high pressure all have relatively low-lying excited states which shift strongly to lower energy with increasing pressure.[12] They also tend to be more strongly self-complexing than the smaller aromatic molecules. It has been postulated[5] that they become reactive at high pressure either by thermal transfer of electrons to the π^* orbital or by increased self-complexing, or a combination of these mechanisms. Similarly, it has been observed[12-14] that the optical absorption peaks corresponding to EDA interaction frequently shift to lower energy (by as much as several thousand cm^{-1} in 100 kbars) with increasing pressure. It is then postulated that the increased thermal occupation of the excited state leads to the reactivity of these complexes.

The first determination of the types of products formed, as presented in this paper, serves a dual purpose. It increases our understanding of electronic processes at high pressure and introduces a new class of organic reaction products.

Experimental Procedure

The perylene used was Aldrich Chemical Co. (purest), sublimed at 150°. The pyrene was from Eastman Kodak Co. and was recrystallized twice from benzene and sublimed at 100°. The iodine was Mallinckrodt reagent grade, sublimed. The complexes were prepared by the method of Kommanduer and Hall.[15] They were stored in a sealed bottle in a darkened desiccator. They were analyzed on formation and just before use. The iodine content was always within 0.5% of the stoichometric value. Although the complexes apparently keep indefinitely, no material more than 3 weeks old was used.

As indicated earlier, the high-pressure cell could hold 2–3 mg of hydrocarbon or 5–6 mg of complex. The samples were held at 160–200 kbars for 24 hr. The pressure was set to be well in the reaction range but below the breaking point of the pistons. In order to accumulate enough material for reasonable separation and characterization (140–180 mg), it was necessary to make 25–30 consecutive runs. The reacted material was stored in a sealed flask in a darkened desiccator.

The separation procedure was in three steps: removal of iodine, removal of products insoluble in benzene, and fractionation of the soluble products by chromatography. The iodine was removed by vacuum sublimation. It came off quantitatively as proved by analysis of the residue. This is of great interest for understanding the reaction process. Evidently, the function of iodine is to provide a low-lying excited state which puts the hydrocarbon into a reactive configuration. The matter is discussed further below.

The soluble material was removed from the residue by multiple extraction with benzene. The insoluble material was subjected to some analysis, but could not be very well characterized. Apparently, it consisted of higher hydrocarbon polymers. It will not be discussed further here.

The soluble material was fractionated as discussed below into monomer and several heavier fractions. The total hydrocarbon gave yields of the following order: 55–60% unreacted monomer, 25% soluble polymer, 15–20% insoluble products.

The fractionation was by chromatography. The product, in 10 ml of benzene, was introduced into a 200-g silica gel column, and gradient elution with cyclohexane, benzene, and ethanol was used in a separation procedure monitered by uv, visible, or nmr spectroscopy. Individual fractions were rechromatographed in preparative tlc silica gel plates. This minimized the possibility of stopcock grease in the product.

There were a number of clear-cut fractions other than the monomer, but for both the perylene and pyrene products only two of these were large enough for satisfactory characterization. In each case we discuss further only these two fractions. It must be well understood that each of these cuts, while quite separated from other fractions, consisted of a group of rather similar materials, rather than a pure component. Any further attempt at fractionation would yield too small an amount for satisfactory characterization. Since the prime interest here is in the *types* of product formed, the study of these fractions is a fruitful procedure. Approximate molecular weights of the products were determined by VPO with a Mechrolab Inc. vapor pressure osmometer, Model 301A. Both of the perylene fractions were in the range 400–550, indicating dimers. The fractions from pyrene gave molecular weights in the range 700–820 indicating tetramers. Accurate molecular weights and some fragmentation data were determined by mass spectrometry. The instrument used was a Varian-MAT Ch-5 mass spectrometer. Samples (0.5–2 mg) were loaded in gold crucibles and run under the following typical operating conditions: acceleration voltage, 3 kV; analyzer pressure, 10^{-7} Torr; electron energy, 70 V. Both oscilloscope and computer output were recorded. The source temperature was 275–325°. The solids probe temperatures used were between 20 and 500°. The results are used later. Here we only indicate that they confirmed the osmometry results.

Infrared spectra were obtained on KBr pellets of the solids using a Perkin-Elmer Model 521 grating spectra photometer adapted for 0.1-mg samples. Uv and visible spectra were taken with a Cary 14 spectrophotometer both with KBr pellets and in solution in Spectrograde cyclohexane.

Esr spectra were taken on a Varian Model V4502 spectrometer with a Model V4522 rectangular cavity. The X-band, used for these samples, had a nominal operating frequency of 9.5 GHz. The field modulation was 100 KHz. Samples were studied in quartz tubes: i.d., 2 mm; o.d., 4 mm. Materials were observed both as solids and in solution. Spectra in solution were taken with benzene as the solvent. The sample size was 2–8 mg. A solid material with a high spin concentration was studied as a small sample because of the short penetration depth of microwaves in a system of high-spin concentration. Spin concentrations are reported as the ratio of the number of spins in a pressed sample to that of an unpressed sample of complex. The two samples were run concurrently. Because of the low-spin concentrations of some samples, cavity and solvent blanks were also recorded with the sample investigated.

Since the characterization depends very heavily on the nmr results which were difficult to obtain, we describe this procedure in some detail. All nmr spectra were taken on a Varian HR-220 spectrometer. For the products, which were less soluble, the technique of computer averaging of transients (CAT) was used. The CAT instrument used was a Technical Measurement Corp. C-1024 transient averaging computer, distributed by Varian.

Samples for nmr were prepared in Spectrograde carbon tetrachloride. The solvent had been passed over an alumina column and was checked for purity with a CAT run prior to use. Solvent

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[12] H. G. Drickamer in "Solid State Physics," Vol. 17, F. Seitz and D. Turnbull, Ed., Academic Press, New York, N. Y., 1965, p 1.

[13] R. B. Aust, M.S. Thesis, University of Illinois, 1962.

[14] D. R. Stephens and H. G. Drickamer, *J. Chem. Phys.*, 30, 1519 (1959).

[15] J. Kommanduer and F. R. Hall, *ibid.*, **34**, 129 (1961).

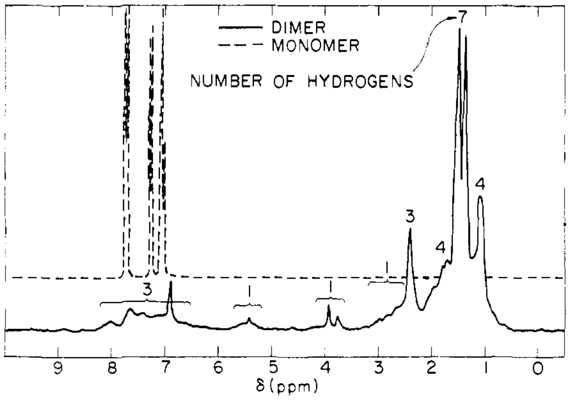

Figure 4. Nmr spectra of the perylene dimer A and perylene.

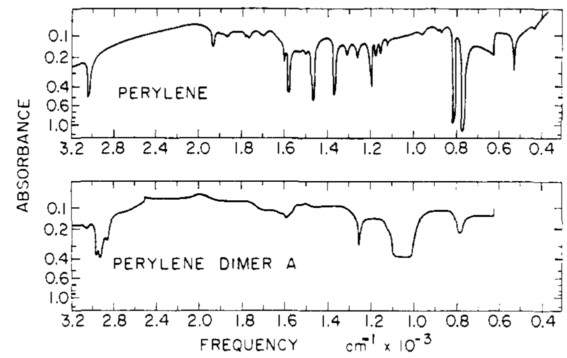

Figure 5. Ir spectra of the perylene dimer A and perylene.

Table I. Structural Features of Products

	Pyrene tetramers		Perylene dimers	
	A	B	A	B
No. of protons	40	40	24	24
Total paraffinic protons	31	30	19	17
(a) Normal ring protons	14	13	7	7
(b) Three-membered ring protons at δ 1.1	5	4	4	4
(c) Protons shifted downfield	12	13	8	6
Total olefinic protons	3	5	2	4
(a) At normal position	0	1	1	1
(b) Shifted upfield by benzene ring	3	4	1	3
No. of aromatic protons	6	5	3	3
Three-membered rings	6	5	5	4
Total aromatic rings	2	2	2	2
Aromatic rings with protons	2	2	1	1
Naphthalene chromophore	0	0	1	1
Total olefin bonds	8	9	4	5
Olefin bonds with protons	2	3	2	3
New bonds	18	17	11	10

blanks were run on the HR-220 with all CAT spectra of products. The solvent always had a peak due to chloroform at 1604 Hz, downfield from tetramethylsilane (TMS). This was used as a reference point for assigning locations to the peaks in the product spectrum. No TMS was used for product spectra.

The sample size used for a CAT run was from 1 to 2 mg, but was larger for single scans of pyrene or perylene. The samples were dissolved in 0.7 mg of solvent and transferred to the nmr tube with a hypodermic syringe. This was done in a drybox whose relative humidity was less than 6%. All samples were dried under vacuum before they were dissolved in the solvent. Syringes and sample tubes were washed with acetone, dried under vacuum, boiled in carbon tetrachloride, and dried again under vacuum. They were then stored in a desiccator under nitrogen atmosphere until used. Because of the size of the samples and the nature of the spectra, it was necessary to scan the spectra 80-150 times in each CAT experiment. The spectrum was generally traced and integrated at two different levels of the CAT memory. Thus, a small peak could be magnified by a factor of 8 over its intensity in the other level of the memory. For each sample of the product, the spectrum was reproduced from three to five times over a period of a month or more. This was done to prove that all peaks were real and of consistent intensity. It also served to show the relative stability of these compounds. The spectra reported are then the result of several CAT runs. The number of protons recorded for each peak has been rounded to the nearest whole number. The actual number, however, differs no more than 0.1 or 0.2 from the number reported.

Characterization of Products

The two classes of products from perylene and the two from pyrene were characterized. We discuss the perylene dimer of type A in some detail, and present a model for it as well as for the pyrene tetramer of type A. The type B dimer and tetramer B differ only moderately from their type A counterparts and will not be analyzed in detail. In Table I we summarize the characteristics of all four products as determined from the spectroscopic studies.

We discuss first the perylene dimer A. It has 19 paraffinic, 2 olefinic, and 3 aromatic protons (see Figure 4). (Resonances in the range 6.6–8.0 ppm downfield were assigned as aromatic, in the range 3.5–5.8 ppm as olefinic, and less than 3.0 ppm as paraffinic.) The olefinic protons were divided into two classes. The proton appearing at 5.5 ppm was approximately in its normal position.[16,17] This proton was not disturbed much by its environment. The proton at 3.7–3.9 ppm was, however, shifted considerably upfield. This shift, nearly 2 ppm, was caused by the location of this proton above the center of an aromatic ring.[16,17] Since three protons were aromatic, only one ring of the outer four in a perylene monomer had a benzenoid structure. This identifies the basic arrangement of the dimer as two skew layers with one olefinic proton positioned over a benzene ring.

The paraffinic protons appear above 3 ppm. Of the 24 protons in a dimer, 19 are paraffinic. In order to have that many paraffinic protons, small rings must be involved in the cross-linking. The highest field protons in dimer A were at 1.1 ppm. For a system with no methyl groups one would anticipate that these would be on three-membered rings.[16,17] It should be noted that, in the absence of proton rearrangement, all paraffinic protons must be tertiary. Some of the protons on a three-membered ring were on carbons also involved in five-membered rings formed by the rearrangement of the original six-membered rings. These appear at 1.5 ppm. For dimer A, there were a minimum of four three-membered rings. Most of the protons appearing at 1.5 ppm were on both three-membered rings and five-membered rings. Those protons appearing between 1.6 and 3.0 ppm were shifted downfield by double bonds or by aromatic rings.

The infrared spectrum of dimer A is reproduced in Figure 5 along with that of the monomer. The following items should be noted. It shows a large amount of paraffinic C–H stretching between 2900 and 3000 cm^{-1}. A small amount of aromatic and olefinic C–H stretching can be observed above 3000 cm^{-1}. Perylene

(16) J. A. Pople, H. J. Bernstein, and W. G. Schneider, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959.

(17) J. W. Emsley, J. Freeney, and L. H. Sutcliffe, "High Resolution NMR Spectroscopy," Pergamon Press, New York, N. Y., 1965.

has a single aromatic stretch in the C–H stretching region. At 1600 cm^{-1} in perylene there is a peak due to C=C vibrations in aromatic rings. This is greatly diminished in both dimers. A broad peak above 1000 cm^{-1} in the spectra of the dimers was due to ring bending in three-, five-, six-, and seven-membered rings. In the ir spectra of some of the products a peak appeared at 1720 cm^{-1} in the region normally associated with C=O stretching. It is possible that some of the soluble products interacted with oxygen dissolved in the solvents used. On the other hand, such peaks occurred also in some insoluble products and in products produced elsewhere[5] which were never in contact with a solvent. The material is, of course, exposed to no oxidizing agent in the high-pressure experiment. Since the presence of a carbonyl bond, formed on handling, on the product would not affect our general interpretation, we do not consider it further.

Uv and visible spectra of the dimer appear in Figure 6. These spectra were taken in solution and are compared with the monomer spectrum. Around 550 to 590 nm there was a small broad absorption. In this area absorptions of excited perylene have been reported along with the absorptions of the reversible dimers of perylene.[18] If this small absorption was caused by P_2^+ there should be a small esr absorption. Esr data indicated a free spin concentration in the sample of approximately 10^{-6} spins per dimer hydrocarbon. At energies above 450 nm there are two absorptions. These are very similar to the π–π^* absorptions of perylene. This would indicate that the molecule has a conjugated π system.

At higher energy, 330 nm, there is a small absorption. If tails from nearby peaks were eliminated, the extinction coefficient of the peak would be about 700. At even higher energy, 280 nm, there is a shoulder representing a buried peak. At 260 nm there is a sharp peak. This is nearly the same location as an absorption in perylene. The two peaks at 280 and 330 nm indicate a naphthalene chromophore. The absorption of the chromophore has been shifted to slightly lower energy by extended conjugation. The peak observed at about 260 nm is believed to be a peak from the two benzene rings in a naphthalene. It has approximately the correct intensity when surrounding absorptions are removed. The anomalous π–π^* absorptions at 400–450 nm were believed to be from a conjugated, but nonaromatic, system of double bonds. The conjugation has been extended beyond that of the olefin system; therefore, the absorption is at a lower energy. The conjugated π system is apparently enlarged with the aid of orbitals from the three-membered rings. It has been pointed out[19] that they appear to be bonded by orbitals of sp^2 and p character, with appropriate symmetry to enter into the π system.

In the mass spectra, peaks are observed corresponding to the monomer (252) and the dimer (502–504). In dimer A, two notable peaks are observed above the monomer. These are at *m/e* 284 and 340. The peak at 340 is from the addition of C_7H_4 to the monomer. For perylene a fragment at *m/e* 87 ($C_7H_3^+$) can be observed. The peak at 284 can not be attributed to an ion which is a monomer plus some other fragment. It is probably a $C_{22}H_{20}$ fragment. This peak is an example of behavior of many alicyclic systems upon ionization. The fragmentation patterns of alicyclic molecules are normally not easily explained, because of the large number of nucleophilic sites.[20]

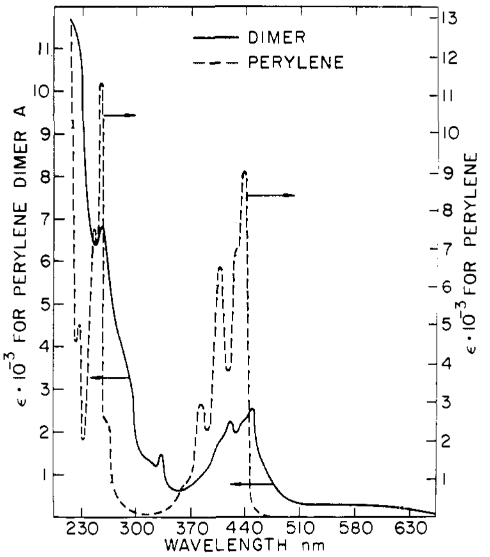

Figure 6. Electronic spectra of the perylene dimer A and perylene.

A model of dimer A has been developed which includes all of the characteristics listed in Table I. It is shown in a stereoscopic representation in Figure 7 and two projections are presented in Figures 8a and 8b. The model consists of two skew monomer layers. The molecule has five three-membered rings, although the nmr spectra, Figure 4, suggests a minimum of four three-membered rings. The predicted spectrum of the model, however, agrees with the actual spectrum since one of the protons at the tip of a three-membered ring is shifted downfield by van der Waals interaction with a nearby carbon. Protons on both three- and five-membered rings, as well as the shifted proton on one of the three-membered rings, would appear near 1.5 ppm. There are ten of these protons. Five of these are shifted downfield by nearby π bonds, but two other protons are appearing near 1.5 ppm due to anisotropies of a σ bond. One olefinic proton, most easily seen in Figure 8b, is positioned approximately over the center of a benzene ring. This proton could well appear slightly above 4 ppm. The other olefinic proton is in the same layer, but it is positioned away from the ring and is assigned a chemical shift near 5.5 ppm.

The top monomer skeleton has four double bonds, which are cross conjugated, and three cyclopropane rings. Two of the three carbons not part of double bonds or the three-membered rings are highly strained. Thus, only one carbon in the top layer of the molecule is not part of a π system of some type. This layer is believed to be the chromophore responsible for the low energy π–π^* absorption.

The other monomer skeleton contains the naphthalene chromophore and two three-membered rings. This naphthalene chromophore is fully conjugated to only one of the three-membered rings. There are 11 new bonds in this model of dimer A. (These appear

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(18) K. Kimura, T. Yamazaki, and S. Katsumata, *J. Phys. Chem.*, **75**, 1768 (1971).

(19) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(20) H. Budzikiewiez, C. Djerassi, and D. H. Williams, "Mass Spectroscopy of Organic Compounds," Holden Day, San Francisco, Calif., 1967.

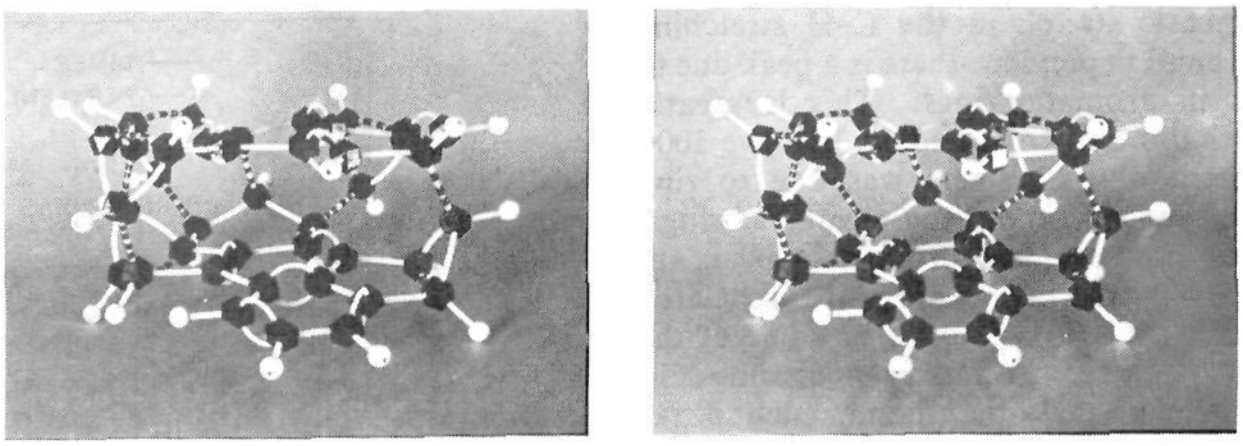

Figure 7. Stereoscopic representation of the perylene dimer A.

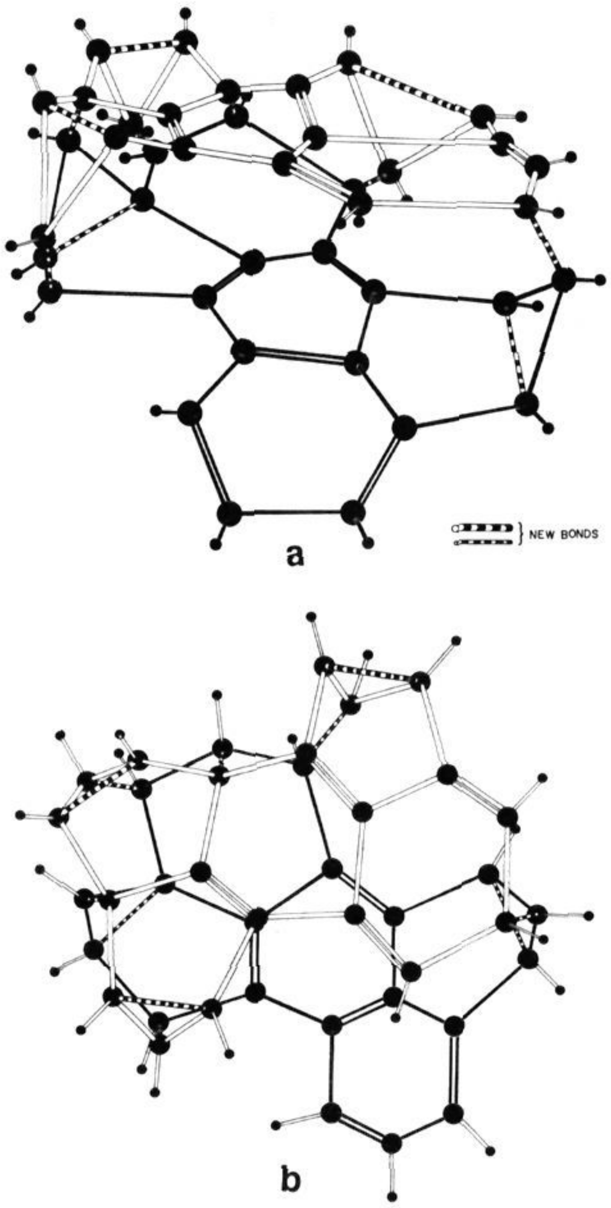

Figure 8. Perylene dimer A: (a) side view; (b) top view.

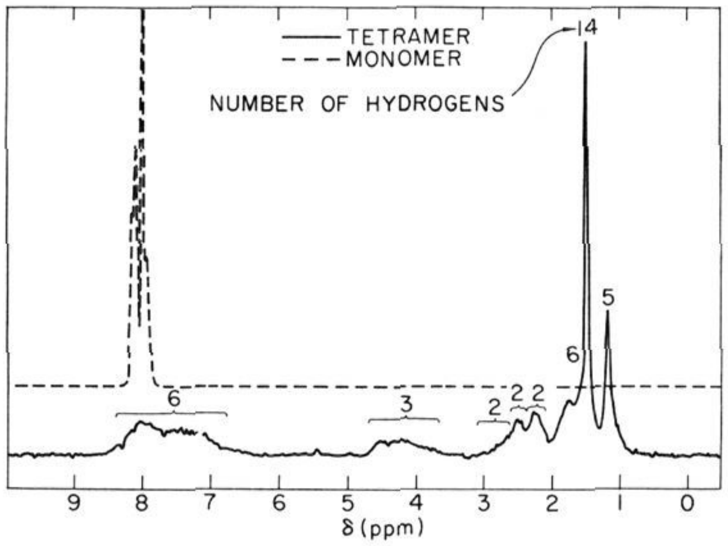

Figure 9. Nmr spectra of the pyrene tetramer A and pyrene.

striped in the figures.) Five of these are part of cyclopropane rings. There are six cross-linking bonds between layers. Since there is one more double bond in dimer B, only ten new σ bonds are formed. Four of these are involved in three-membered rings and six connect the monomer layers. This model discussed above represents the characteristics displayed by the nmr spectra of dimer A, as well as the uv and visible spectra. It is intended as a possible structure for a member of a new class of compounds formed under high pressure. Other models have been constructed; however, the one presented here fits the data observed best. These other models are similar and may also represent molecules actually present in the mixture. Models have also been constructed representing dimer B. Both products are similar, so these will not be presented here.

We turn now to the pyrene tetramer A. The mass spectral measurements give measurable mass at 802–808 confirming the vapor-phase osmometry molecular weight determinations. The nmr spectrum of tetramer A is given in Figure 9. The analysis is similar to that given for the perylene dimer. (We discuss briefly both tetramer A and B since a comparison of the properties is of interest.) The aromatic portion of the spectra indicates that at least two aromatic rings are present. The rings involved for the two products are not the same, however. Tetramer A has six aromatic protons. Tetramer B contains five. For tetramer B this can only mean that just two rings of the monomers are still aromatic. In pyrene two of the four aromatic rings have two protons and the other two have three protons. For tetramer A, the six protons could result from either two or three rings. If three rings were involved, the nmr spectrum of the tetramer would be changed considerably. There would be fewer paraffinic protons, and a larger fraction of these protons would be shifted downfield by the aromatic rings.

The olefinic portions of the spectrum are similar to that of the perylene dimers. In tetramer A, there are three olefinic protons. These are shifted upfield about 1–1.5 ppm from their normal position. The geometry of pyrene is such that two of these protons would be on one double bond with a third proton attached to a second bond. These protons would be positioned 2–3 Å above or just inside the edges of the two benzene rings. In tetramer B there are five olefinic protons. Four of these are shifted upfield by a nearby benzene ring. Two of these protons are over the center of a ring while the two others are positioned above an edge. At the minimum three double bonds involve protons.

In tetramers A and B, out of a total of 40 protons, there are 31 and 30 paraffinic protons, respectively. In the first tetramer at least five of these protons are on the

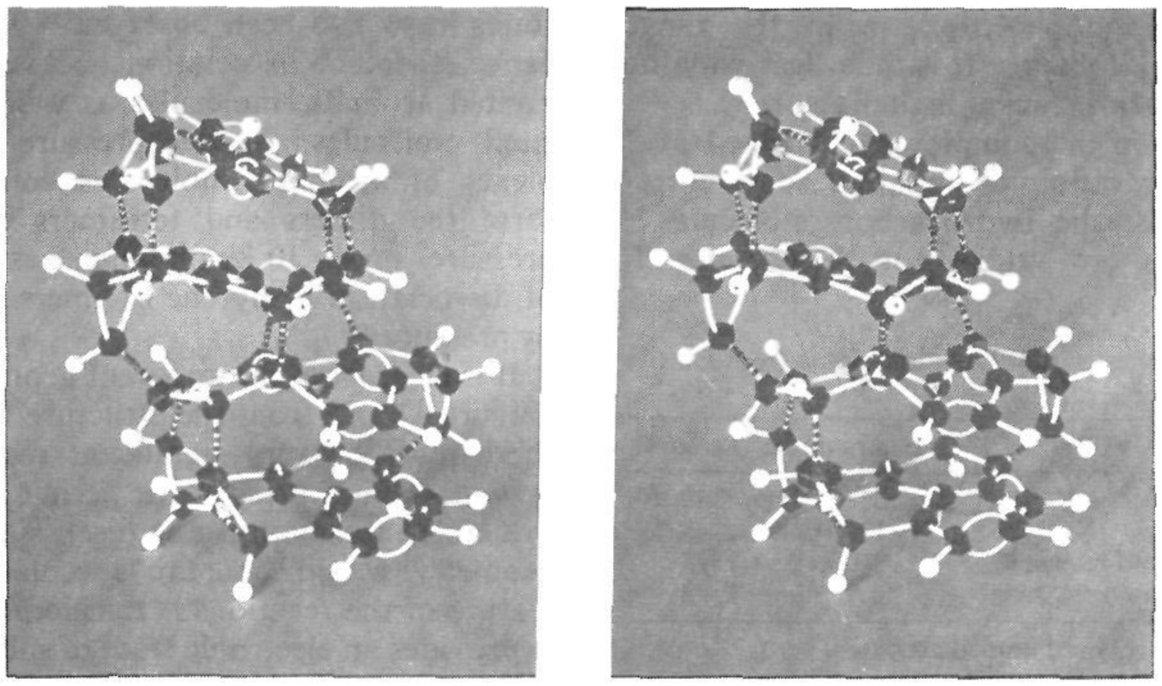

Figure 10. Stereoscopic representation of the pyrene tetramer A.

carbons isolated on three-membered rings. At least four three-membered rings are contained in tetramer B. In tetramer A 14 protons are in a peak found at 1.5 ppm. Twelve protons are in a similar peak in the second product. The explanation for the tetramers is similar to that for the dimers, except that many of these protons are not on carbons part of three-membered rings but are protons shifted upfield by diamagnetic effects of double bonds and benzene rings. The explanation of the other peaks between 1.5 and 3.0 ppm is the same as for the perylene products. All nmr spectra are very similar. The tetramer contains relatively fewer three-membered rings than the dimer, but this is the major difference noted.

The analyses of the ir, uv, and visible spectra were of auxiliary use as they were for the perylene dimer, but they are not presented here. The mass spectra showed definite peaks at 602, 400–403, and 200–202, indicating that the tetramer retained a distinct "memory" of the monomeric structure. The properties determinable from the spectroscopic analyses are listed in Table I.

In Figure 10 we exhibit a stereoscopic representation of a model which fits these characteristics. The tetramer model consists of four skew monomer-like layers, which are turned as much as 90° from being aligned with each other. The layers are also shifted from a vertical position with respect to each other. Therefore the model has a leaning appearance. As explained from mass and electronic spectra the monomer layers are distinct. The σ bond structure of the molecule has not been altered, but many π bonds have been broken and rearranged into three-membered rings and cross-links between layers. The model contains six cyclopropane rings. One proton on a carbon at the tip of a three-membered ring is shifted downfield to about 1.5 ppm by van der Waals interactions with another proton. Two three-membered rings are in each layer containing a benzene ring. These layers are the top and bottom layers of the tetramer. The two benzene rings are part of a styrene chromophore which is shifted to lower energy by the two three-membered rings in each layer.

There are two double bonds which have protons attached to them. These protons are over the edges of the benzene rings. The double bond containing two protons is in the ring of a monomer which has only two protons. The other olefinic proton is on a ring which has three protons. A number of paraffinic protons, shifted downfield by a neighboring double bond, are shifted upfield an equal amount by diamagnetic effects from a benzene ring or combinations of benzene rings and double bonds. These protons, those unshifted by double bonds, the proton from a three-membered ring shifted downfield by van der Waals interactions, and those on both three- and five-membered rings add up to 14. These appear at 1.5 ppm. Other protons are shifted downfield by double bonds or benzene rings and are not shifted upfield very much by diamagnetic or anisotropic effects. These appear between 1.6 and 3.0 ppm. They total 13 protons. Eighteen new bonds are formed in tetramer A; 12 of these are between layers. Seventeen new bonds are formed in tetramer B; 12 of these are also between layers.

Discussion

As mentioned in the introductory section, a common effect of pressure is to shift the energy of one type of orbital with respect to another. Equation 1 evaluates the conditions under which one might expect thermal occupation of the excited state. The CT peak in the pyrene–$2I_2$ complex is located 2.96 eV at 1 atm and has an estimated half-width of 0.7 eV. The presence of the large absorption for I_2 makes it impossible to follow the shift with pressure. However, data for a variety of CT peaks under pressure[12–14] indicate that shifts to lower energy of 0.3–0.6 eV in 100 kbars are common, accompanied by broadening of 10–50%. Using eq 1, it can be shown that a shift of 0.5 eV accompanied by a broadening of 10–15% would reduce E_{th} to zero. A broadening of 30% with little or no shift would also accomplish this. It is clear that thermal occupation of the excited CT state with pressure is entirely feasible. Since the CT peak of the perylene complex apparently lies at lower energy, its occupation at high pressure is also very probable.

On the other hand, the peaks of pure pyrene and perylene are relatively narrow (0.1–0.2 eV). While there is evidence they shift rapidly to lower energy with pressure,[21] no reasonable amount of broadening would

(21) H. W. Offen and R. A. Beardslee, *J. Chem. Phys.*, **48**, 3585 (1968).

permit significant thermal occupation in the range below a few hundred kilobars. It is thus clear why the pure hydrocarbons do not react at high pressure.

Esr measurements on the complexes as formed at 1 atm indicate a concentration of unpaired spins corresponding to 5–7% of the hydrocarbon molecules.[22] Table II summarizes esr studies for the pyrene–$2I_2$ complex on pressed pellets after release of pressure. One sees that at high pressure (80 kbars) the relative fraction of unpaired spins has increased by a factor of 3. However, further increase of pressure, or extended time at high pressure, decreased the unpaired spins as reactions proceeded. After removal of the I_2, there was no more than 0.2% unpaired spin. Most of this decrease in spin concentration is due to decoupling of hydrocarbon and I_2 as occurs when an unreacted complex is decomposed at 1 atm. (This normally gives zero unpaired spins.) It is possible that interaction with oxygen also occurs as discussed earlier, but we do not feel that this is a major factor.

Table II. Relative Concentration of Unpaired Spins from Esr Data (Pyrene · $2I_2$)

	Hours under pressure	
Material	0[a]	24
Unpressed complex	1.00	
Pressed to 80 kbars and released	3.03	1.98
Pressed to 165 kbars and released	1.93	1.72

[a] Taken to pressure and released immediately.

The reactions discussed here proceed through the excited state of the complex. The reaction mechanism could go either through the charged aromatic donors or through an uncharged excited state produced, when an electron in the charged excited state of iodine returns to the aromatic molecule. A number of observers have reported reversible dimer formation in pyrene and perylene systems under a variety of conditions.[23,24] The reversible dimers formed are generally of the Ar_2^+ type, although dimers of the configuration Ar_2^{2+} have been observed, as well as uncharged excimers of the type Ar:Ar*.[23,24] Excimers involving higher excited states have also been observed.[25] There is ample evidence, then, of associations between excited and unexcited aromatic molecules as well as between two excited molecules. Under pressure these excited complexes of aromatic molecules could react further to form the dimers and tetramers discussed here. At pressures under 10 kbars Offen has shown that the rate of dissociation of pyrene excimers is strongly inhibited by pressure.[26]

It is clear from the apparent geometry of the complex (Figure 1) and from the structure of the products that there must be very significant rearrangements in the system at high pressure to permit reaction. With the available information any discussion of the changes in geometry would be pure speculation. The essential feature of the reactions is that iodine acts as a catalyst. It provides an electronic state of such a character that at high pressure the hydrocarbons are placed in a reactive configuration, although it apparently does not participate directly in the reaction; certainly it is not in the final product.

These results indicate that it is possible to synthesize new hydrocarbons in the solid state by applying very high pressure to CT complexes with iodine as an acceptor. The mechanism is the creation of a new ground state for the system by pressure-induced shifts of the electronic energy levels. This is the same mechanism which causes drastic changes in the chemical and physical properties of alkali, alkaline earth, and rare earth metals and compounds of iron. It might be possible to synthesize a number of desired products at high pressure by utilizing complexes with the appropriate geometry and electronic structure.

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