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Pi Electron Systems at High Pressure

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The study of crystals of organic molecules is somewhat less advanced than that of simple inorganic crystals, in part due to the lower symmetry of the organic crystals. However, systems such as aromatic hydrocarbons, involving π orbitals, frequently offer sufficiently simple local symmetry and interesting interactions to study. Figure 1a illustrates a typical π orbital system. At one extreme, crystalline benzene and, at the other extreme, graphite offer prototypes of these systems.

In this paper (*1*) I discuss optical and electrical measurements on these crystals to pressures of several hundred kilobars (1 kilobar equals 986 atmospheres). Emphasis is on irreversible phenomena which illustrate a type of reactivity of π orbitals at short interatomic distances which has not hitherto been expected.

Characteristically, molecules or complexes having this electronic arrangement crystallize in a layered structure, either in a series of planes, as in graphite (discussed at the end of this article), or in a "herringbone" structure having rows of parallel molecules, but with adjacent rows at an angle. In either case the π orbitals abut against each other, and their overlap increases rapidly at high pressure. A number of the phenomena discussed depend on this fact. The discussion is conveniently divided into three sections: pure hydrocarbons, complexes, and graphite.

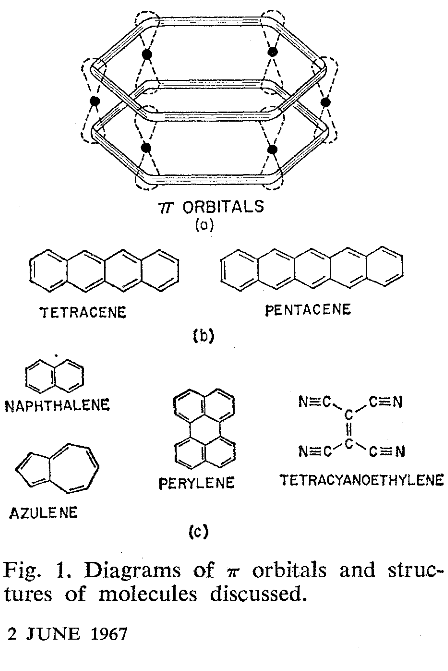

Fig. 1. Diagrams of π orbitals and structures of molecules discussed.

Hydrocarbons

Among the pure hydrocarbons I discuss primarily pentacene, for it has been most thoroughly studied (*2*), although a number of other hydrocarbons exhibit similar behavior. The carbon skeletons of pentacene and tetracene are shown in Fig. 1b.

The optical absorption band of lowest energy in crystals of aromatic hydrocarbons moves to lower energy with increasing number of rings, from benzene through naphthalene, anthracene, tetracene, and pentacene, as the π electrons are conjugated around increasingly longer pathlength. It is a singlet-singlet transition classified as ^1L_a in Platt's nomenclature (*3*).

Figure 2 shows the shift of this low energy-peak in pentacene, tetracene, and anthracene, plotted against density. [The densities are obtained from a generalized curve for p versus ρ/ρ_0 estimated by Samara and Drickamer (*4*).] The close agreement between two of the compounds is probably coincidental. The significant feature is that the peak energy changes more rapidly than linearly with density. The most probable cause is an increased dipole moment for the excited state, corresponding to an increase in charge separation with increasing pressure. A rather gross extrapolation indicates that the transition energy would be zero somewhere just above 200 kilobars. This point is significant in connection with the data for electrical resistance which are discussed below.

The resistivity of a solid can be represented by the equation:

$$R = 1/n\mu e \qquad (1)$$

where n is the number of carriers, μ is their mobility, and e is their charge. For insulators or semiconductors of sufficiently high resistance it is assumed that the limiting step is carrier production and that this is an activated process. One then obtains:

$$R = R_0 \exp{(E/RT)} \qquad (2)$$

For an intrinsic semiconductor, E is equal to half the energy gap between the conduction band and the valence band. In view of the relatively complex structure, the narrow bands, and the difficulty in making ultrapure organic crystals, the results here are expressed in terms of the empirical activation energy E.

In a simple metal, the controlling factor in the resistance is the mobility, which for lattice scattering gives a resistance increasing linearly with temperature. In this discussion I use the term "metallic" to describe a phase

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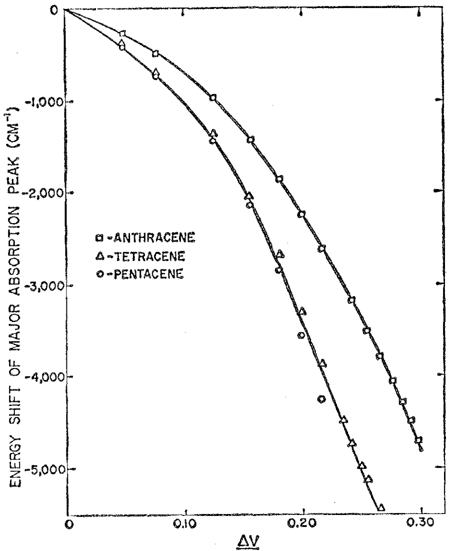


Fig. 2. Peak shift versus fractional-volume change: anthracene, tetracene, and pentacene.

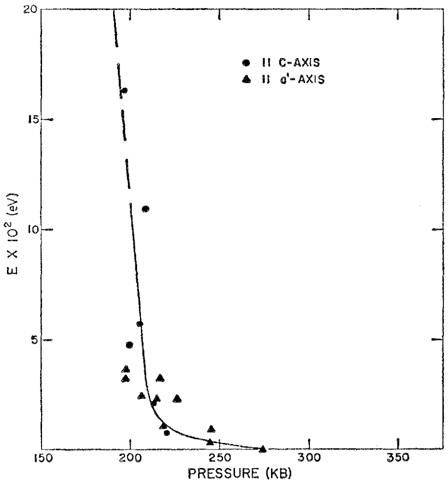


Fig. 4. Activation energy versus pressure: pentacene.

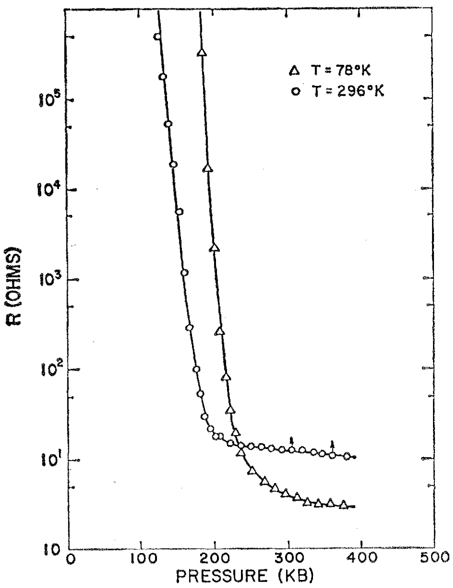


Fig. 3. Resistance versus pressure: single-crystal pentacene (parallel to *c*-axis).

of relatively low resistance which increases reversibly with increasing temperature.

Pentacene crystallizes in the triclinic structure with a well-developed 001 face (perpendicular to the *c*-axis). Resistance measurements were made along this axis and perpendicular to it in directions called *a'* and *b'*, which are not true crystallographic directions.

Figure 3 shows isotherms at 300° and 78°K measured parallel to the *c*-axis. (Isotherms measured in the *a'* and *b'* directions did not differ significantly.) The 78°K isotherm shows a decrease of resistance by about a factor of 10^{16} from 1 atmosphere. (The last six orders of magnitude could be observed in our apparatus.) While the change in resistance with pressure decreases at high pressure, in view of the decreased compressibility, the resistance-density curve may not be far from linear. As long as the temperature is kept below about 180°K the behavior is entirely reversible. Figure 4 shows the activation energy E plotted against pressure. It goes to zero at about 270 kilobars, not far from where the transition energy for the first optical absorption peak extrapolates to zero. At higher pressures the behavior is metallic—that is, the resistance increases with temperature. Thus a metal has been made from an insulator, reversibly and without phase change. Similar behavior has been shown for iodine and stannic iodide (*5*).

The 300°K isotherm reveals a new and unexpected phenomenon. The resistance drops rapidly and reversibly with increasing pressure to about 180 to 200 kilobars. Above 200 kilobars the resistance is almost independent of pressure and drifts upward with time at any pressure. Upon release of pressure the resistance increases much more rapidly than it decreases under increasing pressure. If a sample is compressed to, say, 500 kilobars at 78°K and heated, it behaves reversibly and as a metal as long as the temperature is kept below about 180°K. If it is heated to a higher temperature the resistance increases irreversibly and the sample then behaves as a semiconductor.

The sample is a fraction of a

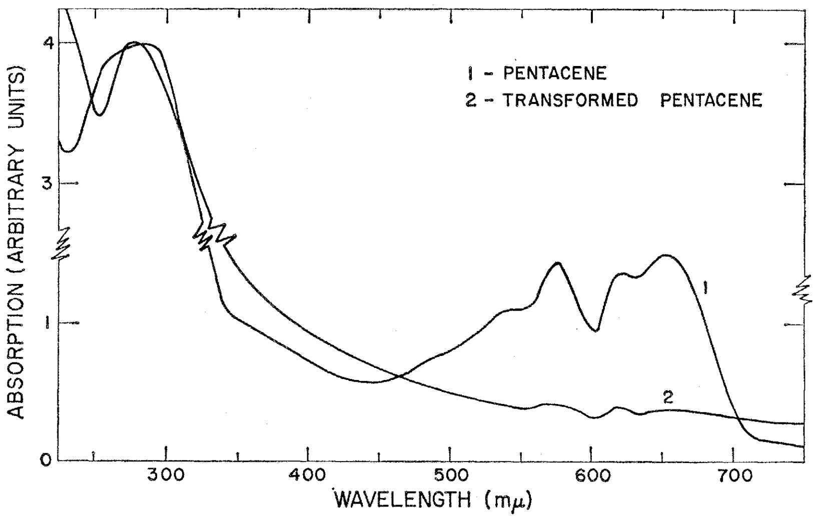


Fig. 5. Absorption spectra; pentacene and transformed pentacene.

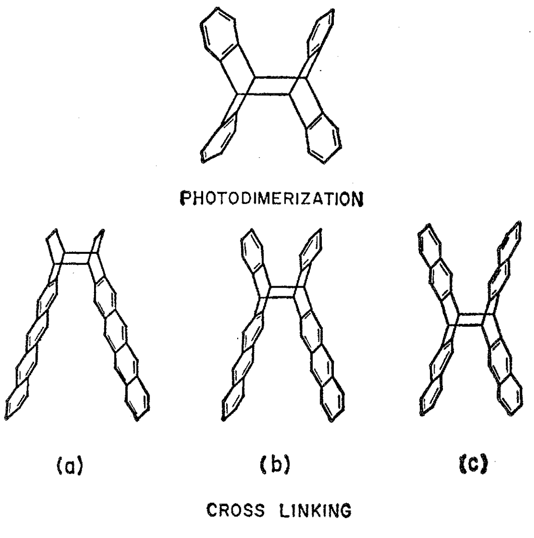


Fig. 6. Diagrammatic representation of photodimerization and cross-linking.

milligram. Hence complete characterization is not yet possible, but some studies have been made on recovered samples. X-rays reveal that the product is still crystalline. It is slightly denser than ordinary pentacene and will not sublime in a vacuum, even at temperatures 100° to 150°C above those at which pentacene normally sublimes. Figure 5 shows the optical absorption spectra of ordinary pentacene and of the product obtained by exposure to 500 kilobars. The absorption peaks of pentacene in the visible spectrum correspond to energy states of electrons conjugated around the entire molecule. The peak at 280 millimicrons is present in benzene and other aromatics and corresponds to states isolated on a single ring. The former type of states are destroyed in the high-pressure product although the latter type remain. Both anthracene and pentacene dimerize photochemically at 1 atmosphere (*6*). It is proposed that high pressure tends to dimerize pentacene (Fig. 6). (Higher polymers are also possible.)

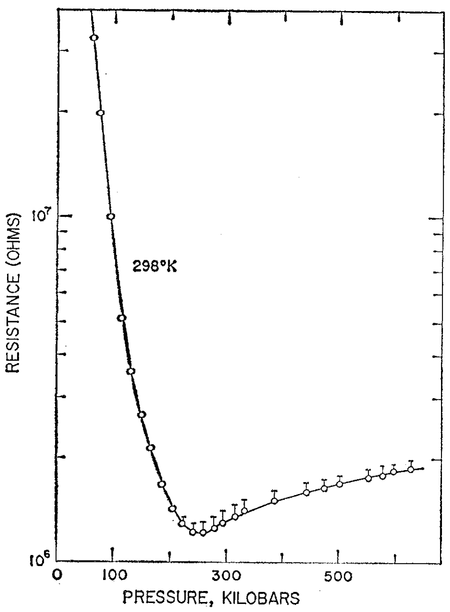


Fig. 7. Resistance versus pressure: tetracyanoethylene-perylene complex (1:1).

Similar behavior has been observed in hexacene and violanthrene, but not in coronene, anthracene, or, probably, tetracene. Apparently cross-linking can occur if there is sufficiently large overlap in area of adjacent molecules.

Complexes

In addition to the hydrocarbons just discussed, pressure effects have been studied on 13 complexes (*7*) of hydrocarbons and halogenated hydrocarbons with such agents as tetracyanoethylene, iodine, *p*-phenylenediamine and its derivatives, and 3,8-diaminopyrene. Studies have also been made (*8*) on tetracyanoquinodimethane and three of its complexes. All these complexes exhibit interesting irreversible behavior, but the complexes of tetracyanoethylene with hydrocarbons and of triethylammonium tetracyanoquinodimethane are discussed here as prototypes.

Figure 1c shows the structure of perylene, naphthalene, azulene, and tetracyanoethylene. All three hydrocarbons form 1 : 1 layered complexes with tetracyanoethylene. The perylene and azulene complexes exhibit a relatively high resistance at 1 atmosphere; the resistance drops many orders of magnitude when pressure is increased to 140 to 160 kilobars. At higher pressures the resistance tends to increase with increasing pressure and to drift upward with time. Figure

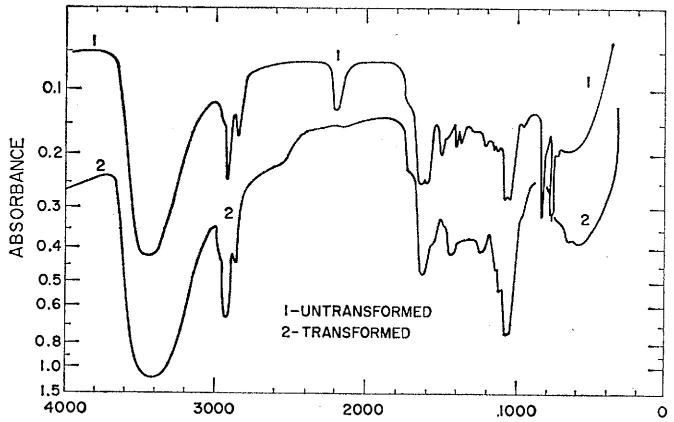
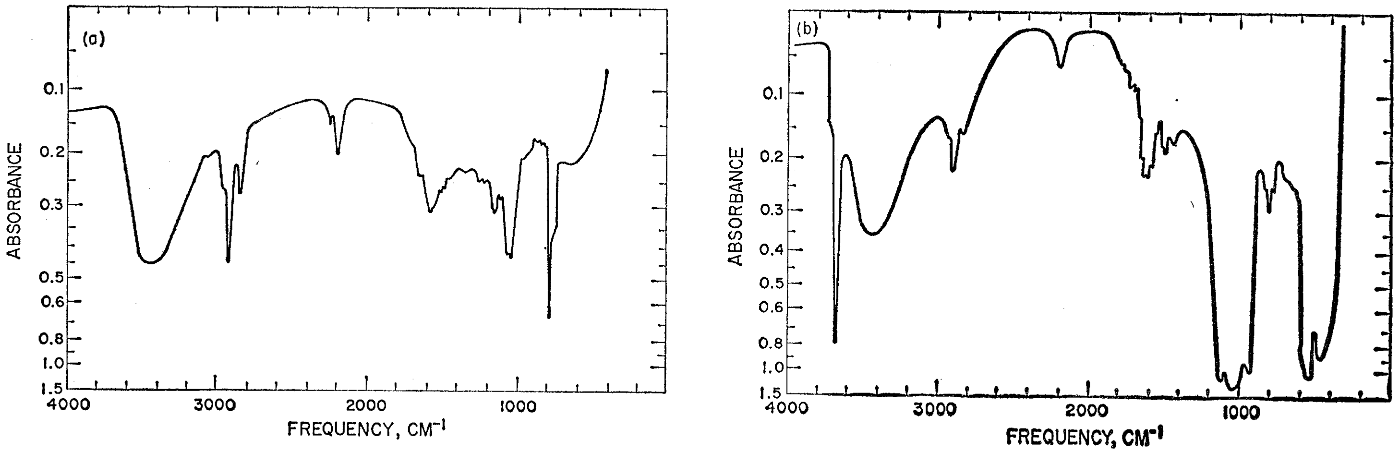


Fig. 8 (left). Infrared spectra of tetracyanoethylene-perylene.

Fig. 9 (below). Infrared spectra of tetracyanoethylene-naphthalene untransformed (a) and transformed (b).



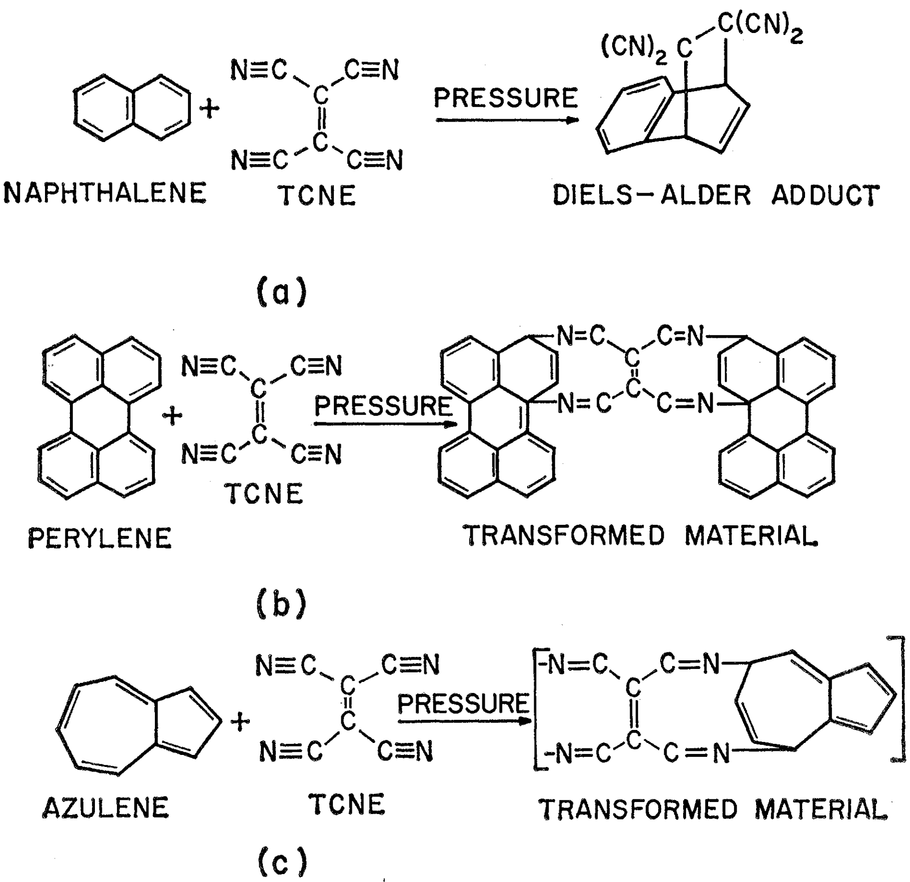


Fig. 10. Possible reactions of tetracyanoethylene complexes.

7 shows typical results for the perylene complex. The behavior above 150 kilobars is irreversible. Again, below about 180°K, the resistance decreases smoothly and reversibly with increasing pressure. There are distinct changes in the electronic spectra in the visible region (the charge-transfer band disappears) but since the transitions are unassigned they are not discussed here. Figure 8 shows the infrared spectra of the perylene complex before and after exposure to high pressure. The C–H and C–C vibrations are unaffected, but the transformed material shows no peak where the $C\equiv N$ stretch appears in the original material. The spectra of the azulene complex are very similar. On the other hand, the spectra of the naphthalene complex are somewhat different. The resistivity of the naphthalene complex is too high to be measured in our apparatus at any pressure, but material was exposed to high pressure and spectra were taken. The behavior of the visible spectra was much like that of the azulene and perylene complexes. Figure 9, a and b, show the infrared spectra; the $C\equiv N$ stretching peak has not disappeared, but there is a drastic change in the region where the C–C stretching and bending frequencies occur.

Figure 10 shows proposed mechanisms for the reactions, based on the very limited evidence available. For the naphthalene complex the most likely mechanism is a Diels-Alder reaction (see Fig. 10a). This sort of reaction is known to take place at 1 atmosphere between anthracene and tetracyanoethylene. For perylene and azulene the principal structural change indicated is the disappearance of the carbon-nitrogen triple bond in tetracyanoethylene. Therefore cross-linking must occur through the cyano groups, possibly as indicated in Fig. 10, b and c. The cross-linking disturbs the π electron distribution, decreasing the portion of the molecule over which the π electrons are mobile. Also, this essentially ionic character of the complex is destroyed. Thus the resistance tends to increase with the extent of the reaction. It would be helpful if the details of crystal structure and arrangement of molecules in these complexes were known, for the type of reaction must depend strongly on the exact geometry. As indicated above, these reactions between hydrocarbons, or halogenated hydrocarbons, and Lewis acids are very general at high pressure.

A very interesting class of organic compounds are the stable complexes involving tetracyanoquinodimethane as the anion. These complexes have very low resistivities—in one case, the lowest yet reported for organic compounds. Their syntheses and properties have been discussed in a series of papers (*9*). Several have been studied at high pressure (*8*), but here I discuss only the triethylammonium complex. Figure 11 shows the struc-

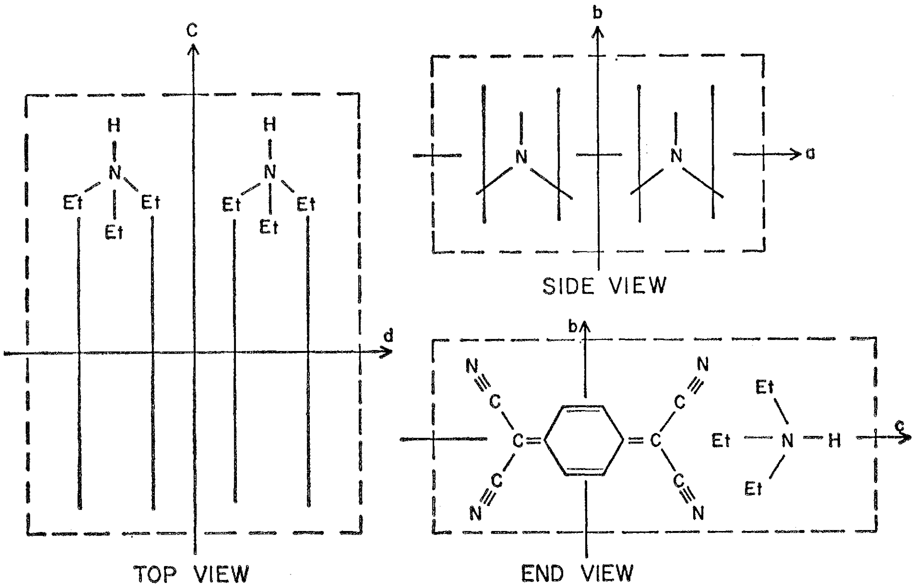


Fig. 11. Structure of triethylammonium tetracyanoquinodimethane. (a) Direction of highest conductivity, (b) direction of intermediate conductivity, (c) direction of lowest conductivity.

ture of the crystal. While the resistance is quite anisotropic at 1 atmosphere, it becomes much more nearly isotropic above about 120 kilobars (Fig. 12). While the initial differences are about 10^4, at 150 kilobars the spread is by a factor of less than 10. Figure 13 shows a room-temperature isotherm taken to high pressure. Above about 100 kilobars there is a distinct tendency for the resistance to drift upward with time; this tendency is accelerated at the higher pressures. The total rise over 500 kilobars is of the order 10^3 to 10^4 and is totally irreversible. In contrast, the 78°K isotherm shows a continuous reversible drop with pressure, leveling at the highest pressures. Again the upper limit for reversible behavior seems to be about 180°K. This feature is shown rather graphically in Fig. 14, an isobar for 128 kilobars. The open circles represent resistance in the reversible region, while the solid dots indicate irreversible behavior. The most obvious change in the visible spectrum is the disappearance of the large charge-transfer peak in the visible. This also occurs in pure tetracyanoquinodimethane. The transformed material is insoluble in boiling acetonitrinile, the solvent used for preparing the complex; and it does not sublime in a vacuum at 370°C, although the untransformed material sublimes rapidly, without decomposition, at 170°C. It appears that what is involved is cross-linking between tetracyanoquinodimethane units, possibly with buckling of the planar molecules and reduction in the free electron character of the π orbitals.

Graphite

In a sense, graphite can be considered as the molecule exhibiting in the most general way a conjugated π electron system. Single-crystal graphite (see Fig. 15a) consists of planes of hexagons with a carbon-carbon nearest-neighbor distance of 1.42 angstroms, very like benzene. The next-nearest-neighbor distance (the lattice parameter a) is 2.46 angstroms. The interlayer separation $c/2$ is 3.35 angstroms. The stacking of the layers is staggered, so that there are two types of lattice sites. Hexagonal boron nitride has a very similar structure (Fig. 15b), except that the layers are not staggered. The properties and behavior of boron nitride are introduced here only insofar as they bear on our understanding of the behavior of graphite.

Single-crystal graphite is a metallic conductor in the planes of atoms and a semiconductor along the c-axis. In contrast, ordinary diamond is a cubic crystal, four-coordinated—that is, it is the prototype of the aliphatic molecule and is an insulator. One then assumes that the binding in the layer is covalent, while the weak interlayer bonding is provided by van der Waals forces. There have been both x-ray (*2*, *10–12*) and electrical studies of graphite at high pressure; and a phase transition has been observed which, I believe, is quite analogous to the irreversible behavior in organic crystals discussed here. I first discuss the effect of pressure on the lattice parameters of graphite and then show how one is led to predict the transition observed.

On the basis of some straightforward thermodynamic arguments (*11*) it can be shown that one can write an equation of state for graphite in the form

$$P = \frac{-dW_{Lc}}{dV} + T\frac{\alpha_c}{\beta_c} \tag{3}$$

where P is the pressure, V is the volume, T is the temperature, W_{Lc} is the cohesive energy in the c direction, and α_c and β_c are the linear coefficients of thermal expansion and compressibility. The second term contributes only a few percent to the pressure and can be approximated in a number of ways. Using a Lennard-Jones 6–12 potential between atoms in adjacent layers, and the lattice sums S_∞ of Girifalco and Lad (*13*), one can write

$$W_{Lc} = \frac{A}{2\sigma(a')^6}\left[\frac{1}{2}y_0^6\ S_\infty^{12}\left(\frac{c}{2}\right) - S_\infty^6\left(\frac{c}{2}\right)\right] \tag{4}$$

Here $1/\sigma$ is the number of atoms per square centimeter in each layer, a' is

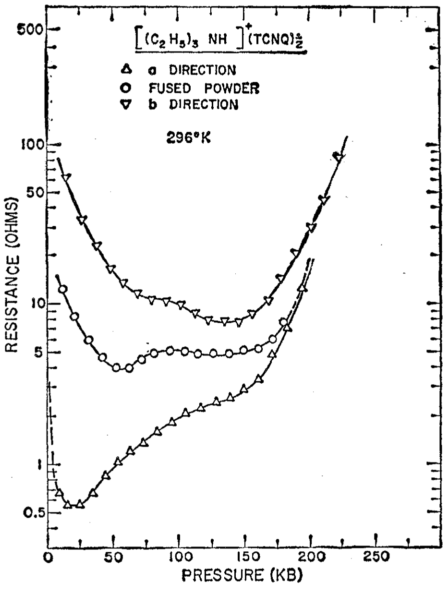


Fig. 12. Resistance versus pressure: triethylammonium tetracyanoquinodimethane; three crystalline directions.

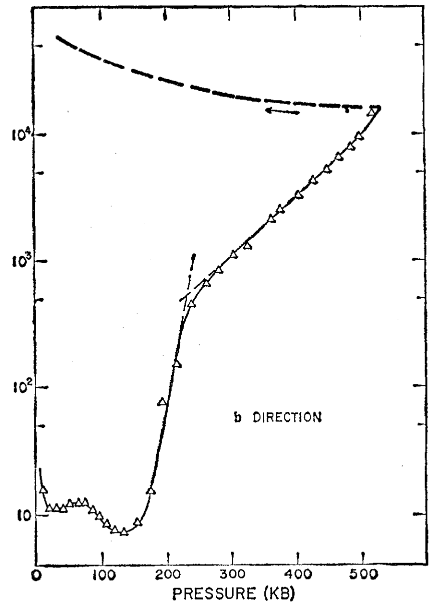


Fig. 13 (center). Resistance versus pressure: triethylammonium tetracyanoquinodimethane.

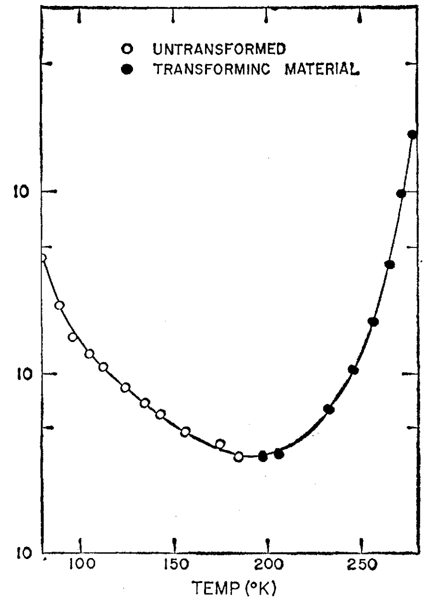
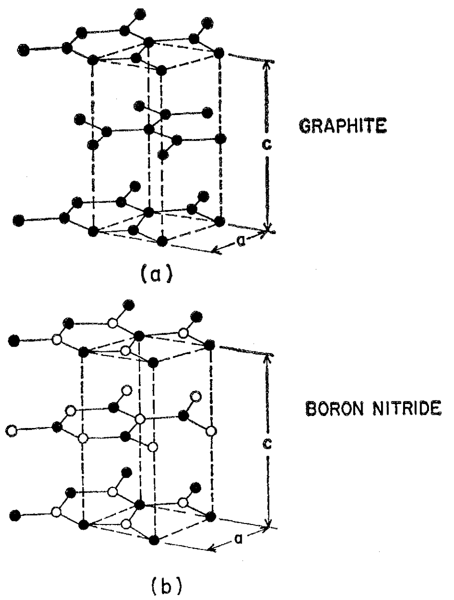


Fig. 14 (bottom). Resistance versus temperature at 128-kilobar isobar: triethylammonium tetracyanoquinodimethane.



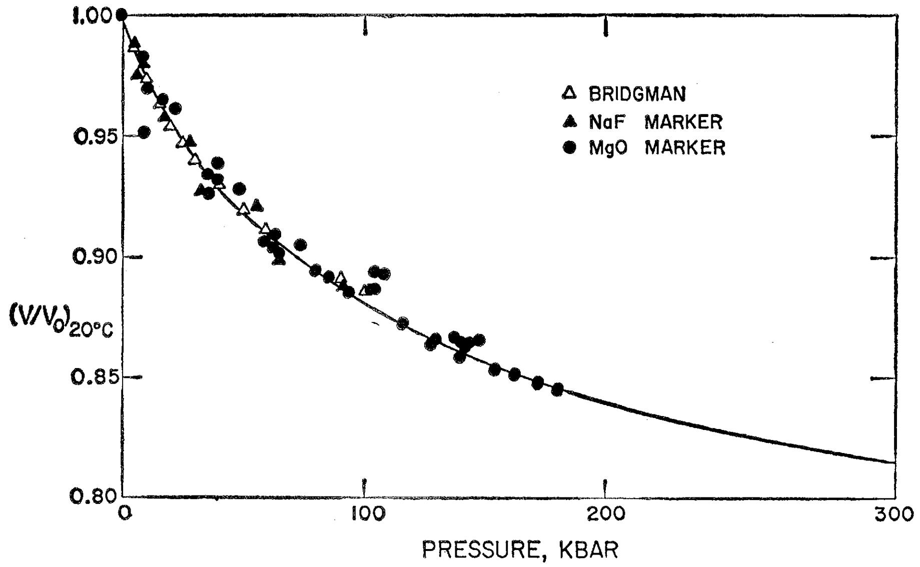
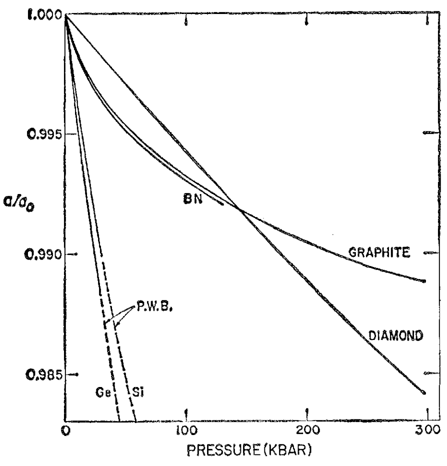
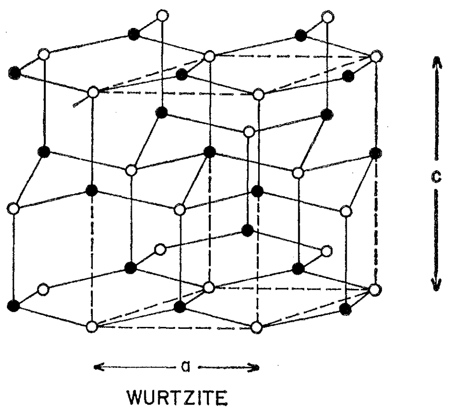


Fig. 15 (above left). Crystal structures of graphite and boron nitride. Fig. 16 (above right). Pressure versus volume, calculated and measured: graphite.





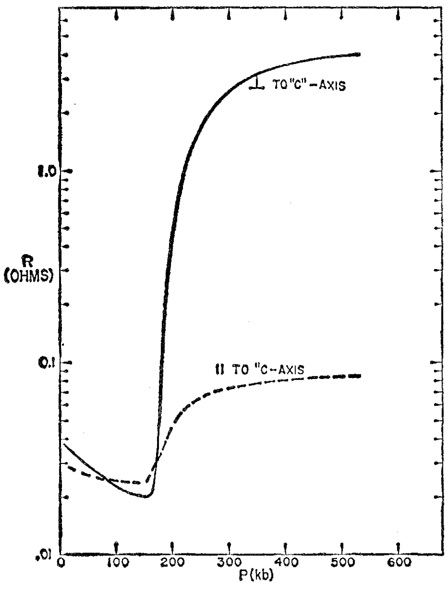


Fig. 17 (left). Linear compressibility a/a_0 versus pressure: diamond, silicon, germanium, graphite, and boron nitride. Fig. 18 (center). The wurtzite structure. Fig. 19 (right). Resistance versus pressure: single-crystal graphite.

the nearest-neighbor distance, and $y_0 = r_0/a'$; A and r_0 are constants which can be evaluated from the initial volume and compressibility. As I have indicated, the lattice sums have been evaluated as a function of interlayer distance. Figure 16 compares the calculated and measured values of volume as functions of pressure and shows that the forces between layers are indeed van der Waals forces.

The change of the a-axis of graphite with pressure reveals a more unexpected phenomenon. Figure 17 compares the linear compressibility of diamond, silicon, and germanium (all having the covalently bonded diamond structure) with the compressibility of the a-axis of graphite and of boron nitride. The linear compressibilities of the first three elements depend only slightly on pressure, whereas the a-axis of graphite is at first much more compressible than diamond and at high pressures much less so. Boron nitride behaves very much like graphite. One would expect the carbon-carbon bond in graphite to be slightly less compressible than that of diamond because of the double bonding, and to show little change in compressibility with pressure.

One reasonable interpretation of the observed result is that the ring is buckling, thus giving the large initial change in a. The effect of puckering in graphite has been measured by Nelson and Riley (*14*), for the case of thermal agitation. The a-axis decreases with increasing temperature to 400°C, above which point it remains roughly constant.

As the pressure increases the rate of buckling decreases because of repulsion between adjacent π orbitals and adjacent layers. At 300 kilobars the carbon atoms are displaced from their equilibrium positions by 0.07 angstrom, 5 percent of the nearest-neighbor distance, or 2 percent of the interlayer distance; displacement results in a 6-degree angle between the carbon p_z orbitals.

Recently Pauling has offered (*15*) a very interesting alternative explanation for the behavior of the lattice parameters of graphite; this explanation has much merit but does not lead so directly to the phase transition that will be discussed now.

Boron nitride, as I have said, behaves very much like graphite. However, at a pressure just over 100 kilobars it transforms to the wurtzite structure (*16*) shown in Fig. 18. One can see that it is very like an array of buckled hexagonal plates. It is of interest to note that the number and geometry of nearest neighbors are the same in diamond as in wurtzite.

Some time ago a first-order phase change was observed (*12*) in single-crystal (or to some extent in pyrolytic) graphite, with a very large increase in resistance, especially in the plane of the hexagons (see Fig. 19). At that time the high pressure phase was not isolated or identified satisfactorily. At 78°K the transition does not occur at pressures up to 500 kilobars. Upon heating at high pressure it is initiated at 180° to 200°K, which is the crucial temperature range for all the organic systems.

Recently "hexagonal diamond" has been identified in the results of shock measurements on graphite (*17*). Bundy and Kasper (*18*) have made a very thorough study of the static conditions for the formation of this analog of wurtzite. It apparently requires a large volume of very precisely oriented carbon atoms, so that it does not occur in powdered graphite. Although the transition runs at room temperature, it is best stabilized by heating to 1000°C after transformation.

I have cited observations of a wide variety of π electron systems in which the molecules are arranged in a layered structure. Rather generally, when the orbitals are brought sufficiently close together, they react and usually destroy the planar symmetry of the molecules. It is interesting, although a little puzzling, that none of these reactions proceed below about 180°K, but that all are initiated at about that temperature. Further investigation along a number of lines is desirable. One should characterize the conditions, mechanisms, and reaction products more thoroughly. A number of these reactions proceed photochemically at 1 atmosphere. It would be useful to relate high-pressure solid-state chemistry to the field of "topochemistry" (*19*)—the investigation of light-induced solid-state reactions in organic crystals. Current Mössbauer studies in our laboratory (*20*) indicate that a wide variety of ferric compounds tend to reduce to the ferrous state at high pressure and room temperature. Many of these reactions occur photochemically at 1 atmosphere also. It would seem that investigation of the relationship between photochemistry and high-pressure chemistry could lead to a less Edisonian approach to the latter field.

References and Notes

1. Work supported in part by the U.S. Atomic Energy Commission.
2. R. B. Aust, W. H. Bentley, H. G. Drickamer, *J. Chem. Phys.* **41**, 1856 (1964).
3. H. B. Klevens and J. R. Platt, *ibid.* **17**, 470 (1949).
4. G. A. Samara and H. G. Drickamer, *ibid.* **37**, 474 (1962).
5. A. S. Balchan and H. G. Drickamer, *ibid.* **34**, 1948 (1961); B. M. Riggleman and H. G. Drickamer, *ibid.* **38**, 2721 (1963).
6. J. Fritzsche, *J. Prakt. Chem.* **101**, 333 (1867); R. Luther and F. Weigert, *Z. Physik. Chem. Leipzig* **51**, 297 (1905); J. B. Birks, J. H. Appleyard, R. Pope, *Photochem. Photobiol.* **2**, 493 (1963).
7. W. H. Bentley and H. G. Drickamer, *J. Chem. Phys.* **42**, 1573 (1965).
8. R. B. Aust, G. A. Samara, H. G. Drickamer, *ibid.* **41**, 2003 (1964).
9. D. S. Acker, R. J. Harder, W. R. Herther, W. Mahler, L. R. Melby, R. E. Benson, W. H. Mochel, *J. Amer. Chem. Soc.* **82**, 6408 (1960); R. G. Kepler, P. E. Bierstedt, R. E. Merrifield, *Phys. Rev. Letters* **5**, 503 (1960); W. J. Siemons, P. E. Bierstedt, R. G. Kepler, *J. Chem. Phys.* **39**, 3523 (1963); R. G. Kepler, *ibid.*, p. 3528.
10. R. W. Lynch and H. G. Drickamer, *J. Chem. Phys.* **44**, 181 (1966).
11. H. G. Drickamer, R. W. Lynch, R. L. Clendenen, *Solid State Phys.* **19**, 135 (1966).
12. G. A. Samara and H. G. Drickamer, *J. Chem. Phys.* **37**, 471 (1962); F. P. Bundy, *ibid.* **38**, 631 (1963); R. B. Aust and H. G. Drickamer, *Science* **140**, 817 (1963).
13. L. A. Girifalco and R. A. Lad, *J. Chem. Phys.* **25**, 693 (1956).
14. J. B. Nelson and D. P. Riley, *Proc. Phys. Soc. London* **57**, 477 (1945).
15. L. Pauling, *Proc. Nat. Acad. Sci. U.S.* **56**, 1646 (1967).
16. F. P. Bundy and R. H. Wentorf, Jr., *J. Chem. Phys.* **38**, 1144 (1963).
17. Netherlands patent release No. 6506395, E. I. du Pont de Nemours and Co., 22 Nov. 1965.
18. F. P. Bundy and J. Kasper, *J. Chem. Phys.*, in press.
19. M. D. Cohen and G. M. J. Schmidt, *J. Chem. Soc.* **1964**, 1966 (1964), and references given therein.
20. A. R. Champion and R. W. Vaughan, private communication.

The Ocean as a Chemical System

Lars Gunnar Sillén

Some 8 years ago I was invited to give a plenary lecture on the physical chemistry of sea water at an international conference on oceanography (*1*). I tried to excuse myself because of ignorance, being no oceanographer but a mere chemist, but the organizers pointed out that I had some experience of the equilibria of ionic solutions. Sea water is obviously an ionic solution, so I was asked to study the subject and tell whatever came to my mind.

This was surely a challenge. The average composition of sea water was easy enough to find in the literature. Table 1 gives the concentrations of the major ions in average sea water of 3.5 percent salinity (content of solid salts). Salinity in the open sea may be varied between 3.2 and 3.75 percent by evaporation or by addition of freshwater (*2*, vol. 1, p. 43); the ratios between the major ions are remarkably constant (*2*, vol. 1, p. 121). The *p*H of the ocean seems to be around 8.1 ± 0.2. Not only is the composition practically uniform, but there seems to be no strong reason to think that it has changed very much during the last few hundred million years.

It was natural for a solution chemist to ask how sea water developed exactly this composition. For instance, how is its *p*H controlled? The standard textbook answer by that time was that *p*H in the ocean is regulated by buffering of the system comprising H_2CO_3, HCO_3^-, and CO_3^{2-}. However, when one begins to think of it one finds that the buffer capacity of the carbonates in solution is pitifully small compared with the amounts of acids and bases that have passed through the ocean system in the course of time. So it seemed to me that either the *p*H of the ocean must be precarious or there must be some other controlling factor. In my 1959 lecture (*1*) I pointed out that the fine-grained silicates (especially the clays) have very great buffering capacity and may well determine the *p*H of the ocean.

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