Table 1. Ambient-temperature phosphorescence spectra of representative compounds absorbed on paper as 4 m*M* solutions in 1*M* NaOH (unless otherwise noted) and dried thoroughly.

Compound	Maximum emission wavelength (nm)
4-Biphenylcarboxylic acid	450 482 500–515
Diphenic acid	490
1-Naphthoic acid	500 530 560–575
Naphthalic acid	497 535 570–585
Napthalene-β-sulfonic acid	495–510 525
1-Aminonaphthalene-4-sulfonic acid	505–555
2-Naphthol-6-sulfonic acid	533
Eosin Y (0.5 m*M*, *p*H 8)	555 680
Auramine O (0.4 m*M*, *p*H 8)	520
Coproporphyrin III (*p*H 8)	582 625 682

list of representative compounds investigated and the corresponding phosphorescence maxima. Characteristic phosphorescence decay times measured by flash photolysis ranged from 0.1 to 0.7 second. In favorable cases excitation with a 15-watt ultraviolet Mineralight produces phosphorescence plainly visible under ordinary room light, and visually observable for over 5 seconds in the dark.

Although we do not understand why surface adsorption should so strongly inhibit the usual processes of nonradiative decay and oxygen quenching, the technique is quite convenient for demonstrating phosphorescence phenomena and obtaining triplet state spectra without the usual requirements of oxygen exclusion or operation at liquid nitrogen temperatures, as well as supplying a simple means for identifying a variety of organic molecules, including many of biological interest. A detailed report of this work is in press (*4*).

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References and Notes

1. M. Zander, *Phosphorimetry* (Academic Press, New York, 1968), p. 117.
2. Polynuclear aromatics have been observed to phosphoresce at 77°K on paper chromatograms [A. Szent-Györgyi, *Science* **126**, 751 (1957)]. Phosphorescence spectra of solutions frozen at 77°K on glass fiber paper, paper, and silica gel have been measured [M. Zander and U. Schimpf, *Angew. Chem.* **70**, 503 (1958); M. Zander, *Erdoel Kohle* **15**, 362 (1962); E. Sawicki and J. D. Pfuff, *Anal. Chim. Acta* **32**, 521 (1965); E. Sawicki and H. Johnson, *Microchem. J.* **8**, 85 (1964)]. There is, of course, extensive literature on phosphorescent emission from trace impurities in host crystals, but we are dealing here with emission from the major component in the system.
3. E. M. Schulman, A. R. Lepley, C. Walling, presented in part at the 13th Annual Rocky Mountain Spectroscopy Conference, Society for Applied Spectroscopy, Denver, Colorado, August 1971.
4. E. M. Schulman and C. Walling, *J. Phys. Chem.*, in press.
5. Supported by a grant from the National Science Foundation. We thank Dr. A. R. Lepley of the Department of Chemistry, Marshall University, for assistance in spectral measurements; Dr. J. D. Spikes of the Biology Department of the University of Utah for the use of his phosphorimeter; and Dr. S. G. Hadley and V. Alvarez of this department for flash photolysis measurements.

22 May 1972; revised 14 July 1972 ■

Carbon: A Suggested New Hexagonal Crystal Form

Abstract. *Evidence for a new polymorphic form of carbon, similar to but distinct from chaoite, has been discovered. It is trigonal, with* $a_0 = 5.33$ *angstroms and* $c_0 = 12.24$ *angstroms. It is produced along with chaoite on the surfaces of graphitic carbons under free-vaporization conditions at low pressures, with temperatures above approximately 2550°K.*

We have found evidence for a new hexagonal form of carbon during our studies of chaoite (*1*). We refer to it provisionally as carbon VI, since graphite, rhombohedral graphite, diamond, lonsdaleite, and chaoite may be regarded as the first five crystal forms of carbon. Carbon VI, if this is indeed its correct identity, is produced under the following conditions. (i) It is formed along with chaoite when graphitic carbons are heated resistively or radiatively above a threshold temperature of ~ 2550°K at any pressure in the range from 10^{-4} torr to 1 atm. These pressures define the range studied and do not necessarily represent stability limits. (ii) Laser heating produces carbon VI in greater abundance than resistive heating (*2*). In fact, material taken from the walls of laser craters yielded the electron diffraction patterns that made it possible to characterize this carbon form. Moreover, laser heating of glassy carbon produced a large number of well-formed single crystals and twins. (iii) A short-duration (~ 0.05-second), 50,000-Å arc between graphitic carbon electrodes produced carbon VI almost exclusively in a very small yield (*3*).

We studied carbon VI entirely by electron diffraction techniques, because all of the crystals were ~ 0.5 μm in their largest dimension and were difficult to separate from graphite and chaoite. An electron micrograph of a twinned crystal of carbon VI is shown in Fig. 1A; a *c*-axis electron diffraction pattern is shown in Fig. 1B. Most of the patterns were single-crystal or twinned crystal patterns; ring patterns were rather rare. Four tilted crystal patterns made it possible to get a value for c_0. The values found for the cell parameters were as follows: $a_0 = 5.33 \pm 0.05$ Å and $c_0 = 12.24 \pm 0.18$ Å. In *c*-axis diffraction patterns of carbon VI, all reflections are present. The *c*-axis diffraction patterns of chaoite, on the other hand, obey the condition $-h + k = 3n$. In addition, the reflections given in Table 1 have been observed in patterns from tilted crystals. We were able to determine the orientation of the axes by correlating electron diffraction patterns with electron micrographs, and we found that alternate edges of the six-sided basal-plane platelets were two types of steep second-order pyramids.

The unit cell dimensions of carbon VI appear to be related to those of lonsdaleite in that a_0 for carbon VI is close to $2a_0$ for lonsdaleite and c_0 for carbon VI is very close to $3c_0$ for lonsdaleite. On the other hand, the lattice parameters of the larger H-cell for carbon VI bear some resemblance to those of chaoite; a_0 is 9.24 Å for carbon VI and 8.95 Å for chaoite, and c_0 is 12.24 Å for carbon VI and 14.07 Å for chaoite. By means of a careful study of the morphology and especially of the twinning of the small crystallites we established that both chaoite and carbon VI belong to point group 3. The space group of carbon VI may be either *P*3 or $P3_{1,2}$ (and the same is true of chaoite). This finding implies that both of these carbon forms may be optically active and pyroelectric, may exhibit the linear electrooptical effect, and may be piezoelectric in all three modes: hydrostatic, compression, and torsion.

Electron probe analysis of single crystals was not possible because of their small size. However, with the Cameca 27-101 electron probe operating in its transmission mode, it was possible to probe on a standard electron microscope grid an area 25 μm in diameter that contained several crystals of carbon VI along with a cluster of chaoite crystals. This area was analyzed for carbon and for silicon, oxygen, aluminum, calcium, iron, and chromium, the elements that contaminate the starting materials. Analyses for tantalum and tungsten were also carried out, since these elements are present in some of the structural parts of the apparatus used to produce the crystals. Carbon gave an average count of 9800 for a 10-second counting period. The background count was 450 over the same period. For the rest of the elements, the count was not significantly above background over the same counting period. These analytical results and the electron diffraction data lead us to believe that the crystals are a new form of carbon.

X-ray diffraction lines of carbon VI are very difficult to find in Debye-Scherrer patterns, because carbon VI occurs in very low concentration and most of its reflections are very close to or coincide with those of graphite and chaoite. However, all samples known to contain carbon VI exhibit a line at 6.0 to 6.1 Å that is believed to be the 00 · 2 reflection.

We know very little about the properties of carbon VI. It has a density greater than 2.9 g/cm^3, and the crystals are optically transparent. There is some evidence that they may be faintly orange-red in macroscopic clusters; however, this coloration could be due to an impurity. The crystals are much more resistant to oxidation and reduction than those of graphite. In general, the properties of carbon VI resemble those of chaoite and diamond much more than those of graphite. Thus far, we have observed only one property of carbon VI that differs from those of chaoite. In an electron microscope, both carbon VI and chaoite are unaffected by a 75-kv electron beam; however, at 100 kv carbon VI quickly shows evidence of damage, as shown in Fig. 1, C and D, whereas chaoite crystals remain unchanged.

Table 1. Electron diffraction data for the new hexagonal form of carbon $(\ell \neq 0)$.

Observed interplanar spacing (Å)	$hk \cdot \ell$
4.30	01 · 1
3.06	01 · 3
2.61	11 · 1
2.44	11 · 2
1.85	01 · 6
1.73	12 · 1
1.62	12 · 3
1.52	02 · 6
1.28	13 · 1
1.21	11 · 9
1.05	23 · 2
1.00	14 · 1
0.876	12 · 12

It may be that carbon VI is not a stable carbon form (it always occurs with chaoite) but rather an intermediate form in the conversion of graphite to chaoite. Alternatively, carbon VI could be an impurity-modified form of chaoite, which would explain the simultaneous existence of two carbon polymorphs that are so similar. In some experiments, carbon VI is accompanied by numerous crystal fragments that exhibit electron diffraction patterns that can be attributed to various superstructures of monoclinically distorted. pseudohexagonal carbon VI. We sup-

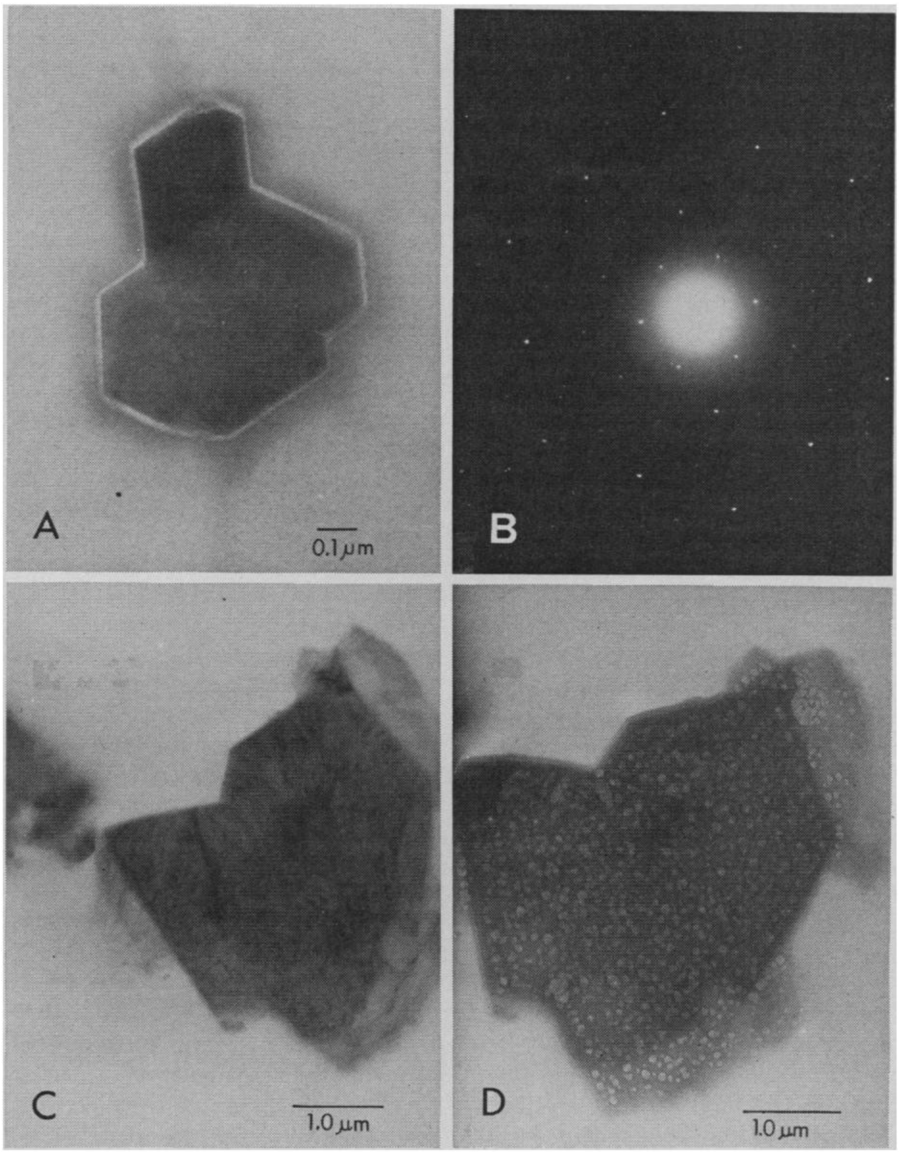

Fig. 1. (A) Electron micrograph of a carbon VI twin obtained from the basal plane edges of resistively heated pyrolytic graphite. (B) The *c*-axis electron diffraction pattern of carbon VI. (C) Electron micrograph of a carbon VI twin produced in the Union Carbide 50,000-Å arc, taken at 75 kv. (D) Electron micrograph of the crystal shown in (C), showing radiation damage produced by a 100-kv electron beam.

pose that, under suitable conditions, carbon VI can serve as a sink for impurities in the system and give rise to various derivative structures. This explanation would lend some plausibility to the speculation mentioned above that carbon VI is itself a modified chaoite.

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References and Notes

1. A. G. Whittaker and P. Kintner, *Science* **165**, 589 (1969); A. El Goresy and G. Donnay, *ibid.* **161**, 363 (1969); A. G. Whittaker, G. Donnay, K. Lonsdale, *Carnegie Inst. Wash. Annu. Rep. Geophys. Lab.* (1969–1970), p. 311.
2. L. S. Nelson, A. G. Whittaker, B. Tooper, in preparation.
3. Samples were obtained through the courtesy of Dr. W. W. Lozier from the high-current arc facility at the Parma Technical Center, Union Carbide Corporation, Parma, Ohio. Only material near the electrode center gave diffraction patterns of the new carbon form.
4. We thank P. Kintner for preparing the material used in these studies and B. Tooper and E. Watts who carried out the electron diffraction analysis and microscopy.

10 May 1972; revised 17 July 1972

Evidence for the Neutral Hypothesis of Protein Polymorphism

Abstract. *Data for some 400 polymorphic proteins were examined with special reference to molecular evolution, by using a statistic that depends on neither mutation rate, population structure, nor other ecological factors. The result indicates that most of these polymorphisms are maintained in a population by mutation and random genetic drift.*

Most authors who have studied protein polymorphisms by gel electrophoresis in various species have concluded that they are maintained by some form of balancing selection. Some of the reasons are: Some species show marked similarity of frequencies of the same allele in widely separated local populations; this has been claimed as evidence for selection [see, for example, (*1*)]. Some species show local and regional differences in gene frequencies; these have been correlated with environmental factors and claimed as evidence for selection [see (*2*)]. The same low-frequency alleles appear repeatedly in different local populations, and this has been claimed as evidence for selection [see (*3*)]. Populations presumed to have different effective numbers have been observed to have a constant number of alleles, and this has been claimed as evidence for selection [see (*4*)]. Closely related species have been found to have the same alleles at a given polymorphic locus; closely related species have been found to have different alleles at other loci; both observations have been interpreted as evidence for the action of selection in evolution.

It has also been argued that these polymorphisms are mainly the consequence of random drift of neutral alleles (*5*). The distribution of neutral alleles in a finite population is known (*6*), and Ewens (*7*) has proposed a method for testing actual data for agreement with this hypothesis. However, this and the various observational methods require assumptions about population size, mutation rate, migration, and breeding structure. Usually the necessary parameters are unknown. A thorough knowledge of the ecology and physiology of the organisms would help solve the problem. An alternative method is to find measurements and relationships that are independent of population structure and mutation rate, and to compare the population data with expectations based on these relationships for various hypothetical mechanisms for maintaining the polymorphism. In this report we use one "invariant" relationship (*8*) in an attempt to discriminate among rival hypotheses.

A new mutant will eventually be fixed in the population or lost by extinction (except for the possibility of entering a stable polymorphism, which will be discussed later). During the process the gene will pass through various gene frequencies. For simple selection or drift in a panmictic population the sojourn time spent in a specified gene-frequency interval (not necessarily during contiguous time intervals, since the change in frequency can reverse direction) can be calculated (*9*). With a complex population structure this is an unknown function of selection, random drift, migration, and the breeding structure. However, Maruyama (*8*) has shown that, whatever the time that a mutant spends at a given frequency, the expected total number of mutant heterozygotes is a simple function independent of the time. It is remarkable that this does not depend on the population structure, provided that the population is not divided into completely isolated groups.

Throughout this report, Y refers to the global gene frequency. The sum of the number of heterozygotes is a function of local gene frequencies.

If the mutant gene is neutral the total number of heterozygotes during the time the mutant is at frequency Y is proportional to $1-Y$. More precisely, the sum of the proportion of heterozygotes during those generations when the mutant gene frequency is in the interval $Y \pm \delta Y/2$ is $4(1-Y)\delta Y$.

If the process has been going on for sufficient time to reach a steady state, the ergodic principle applies and we can regard observations of many mutants at one time as equivalent to observing a single mutant for a long time. Therefore, if we examine a group of populations whose mutant frequencies are within some specified range around Y we should expect the sum of the proportion of mutant heterozygotes to be proportional to $1-Y$.

A practical difficulty is that when we observe a heterozygote AA' we do not know whether A or A' is the mutant. However, if the frequency of A is Y, that of A' is $1-Y$. We therefore reflect the gene frequency scale around the value of 0.5 so that heterozygotes corresponding to the gene frequencies Y and $1-Y$ appear at the same abscissa when the data are graphed. The ordinate is the number of heterozygotes, which will be the sum of the two values $4(1-Y)$ and $4[1-(1-Y)]$, which is simply 4. The sum of the proportion of heterozygotes in populations with a given gene frequency is a constant, independent of the gene frequency. This provides an opportunity to test the neutral hypothesis.

A second possibility is that the mutant gene is favorable. Assume that it has a selective advantage s in heterozygotes and $2s$ in homozygotes. Then the frequency of heterozygotes during the time that the mutant is at frequency Y is

$$\frac{2S(1-Y)S(1/2N)}{sS(1)}$$

where $S(z)=1-\exp(-4Nsz)$. A derivation of this formula is given in Maruyama (*8*). For small s and $4Ns \gg 1$, $S(1/2N)=1-\exp(-2s)\approx 2s$, $S(1)\approx 1$, and the heterozygote frequency is approximately 4 for all except very small values of Y. Neutral mutations and beneficial mutations without dom-