The structure of a new cubic form of carbon

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The structure of a new cubic form of diamond-like carbon, obtained by heating amorphous carbyne on the surface of materials with cubic crystal lattices, was investigated. This form was shown to have a well-like structure.

Key word: carbon, carbyne, diamond, allotropic modifications of carbon.

Previously[1] we obtained a new cubic form of carbon, which, according to the type of bond (sp^3) present, can be assigned to the diamond family. The density of this carbon is about half that of diamond (~1.6). Its IR spectrum exhibits absorption bands typical of diamond (1336 cm^{-1} and 1582 cm^{-1}).

In this work, we present new data concerning the structure of the new form of carbon.

The polycumulene form of carbyne is transformed into diamond even under ambient conditions in the presence of ultradisperse diamond (UDD).[2] The reason for this easy transformation is the structure of the polycumulene chains and the fact that regular "crosslinks" appear between them when they are heated slightly.

When amorphous carbyne, prepared by chemical carbonization of polyvinylidene halides, is heated (in a glass tube or in a metallic crucible) on the surface of a material with a cubic lattice (NaCl, Si, Me, *etc.*) at 130 °C, it crystallizes in such a way that arbitrarily oriented zigzag-shaped carbon chains are arranged strictly perpendicular to the surface.[3] Increasing the temperature to 360 °C causes these oriented chains to become linked at the break points, where cleaved bonds occur (for the valency of a carbon atom to be saturated, eight carbyne chains must be located close to one another). The cube thus arising retains its zigzag-like structure until cleavage of the double bonds and the formation of interchain crosslinks, accompanied by additional heat evolution, begins. Consequently, a new diamond-like carbon, having the structure of a well is formed (Fig. 1). The structure of this new quasi-unidimensional diamond is confirmed by its X-ray diffraction parameters: $a = b = c = 3.028$ Å, $\varphi = 90°$, $\lambda = 1.54$ Å, $\rho = 1.6$. The depth of the well depends on the length (mol. weight) of the polycumulene chain taken. The new carbon, like diamond, is resistant to oxidizing reagents; therefore, it can be purified by boiling in hydrochloric, nitric, or sulfuric acid. It is insoluble in hydrofluoric acid. Its crystals are optically transparent in the visible and infrared regions.

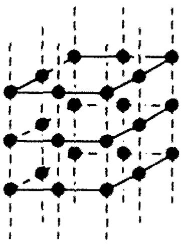

Fig. 1. Structure of the new cubic carbon (a well).

The low density of the new carbon is due to the presence of empty space. Its hardness is not lower than that of diamond (>9 MOHS).[5]

The presence of a regular zigzag in the carbyne chain is the crucial factor responsible for the formation of the new cubic carbon or diamond from it. It determines the step in the regular crosslinking, so that crosslinks arise in strictly specified positions rather than in random positions.

We now discuss yet another surprising experiment, which is easy to explain from the above standpoint, *viz.*, the preparation of cubic carbon from cellulose.

Cellulose is a rigid-chain crystalline natural polymer with strong intermolecular hydrogen bonds. The primary components of its supermolecular structure are microfibrilles having a helical shape. Thermal destruction starts at 150 °C (as this takes place, fibrilles orient themselves at right angles to the plane) and affords a product with a system of conjugated double bonds, as follows from both published data and our data.[4] The IR spectrum of the black intermediate formed during the pyrolysis of cellulose exhibits bands in the 1100—1700 cm^{-1} region, typical of zigzag-shaped carbon chains resulting from the chemical carbonization of polyvinylidene halides (Fig. 2).

Above 300 °C, the double bonds formed start to cleave with evolution of additional heat to give white carbon, whose X-ray diffraction pattern is identical to

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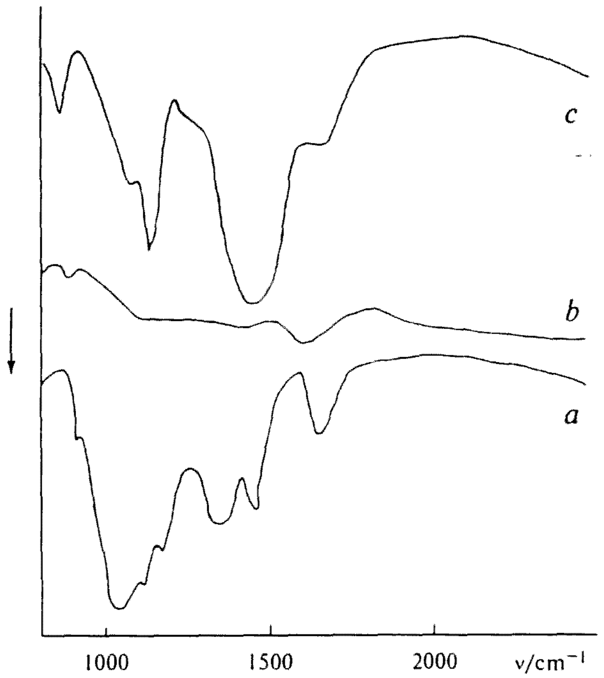

Fig. 2. IR spectra: initial cellulose (*a*); the intermediate black product of the pyrolysis of cellulose (*b*); the final white product of the pyrolysis of cellulose (*c*).

that of the carbon formed during heating of polycumulene.

A typical peak corresponding to an interplanar distance of 3.18 Å was also found in the X-ray diffraction pattern of polyethylene carbonized under similar conditions (Fig. 3).

Experimental

IR spectra of the samples were recorded on a UR-20 two-beam spectrophotometer.

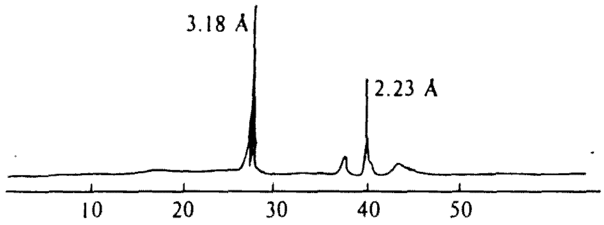

Fig. 3. X-ray diffraction pattern of the product of pyrolysis of polyethylene

X-ray diffraction patterns of the samples were obtained on a DRON-3 diffractometer.

Carbyne samples were obtained by dehydrochlorination of PVDC by a previously described procedure.[3] The amorphous powder was heated in a quartz tube in an argon flow at 360 °C. Discoloration of the black powder indicated completion of the reaction. The yield of the white product was no more than 15% of the starting carbynoid.

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