4.3. CARBYNE INTERCALATION COMPOUNDS

I.A. UDOD
Department of Chemistry, 
M.V.Lomonosov Moscow State University, 
Moscow 119899, Russia

Abstract - Structural data about linear carbon modifications within the span of more than 30 years of rather ‘mysterious’ carbyne history were analyzed. A two-dimensional structure with a hexagonal parameter \( a = 505-525 \) pm is considered the basis for all carbyne modifications. The large value of this parameter, larger than a 300 pm-van der Waals diameter of \( sp \)-carbon atoms, is accounted for by the existence of regular vacancies. The three-dimensional packing of zigzag-like carbon chains with a \( 3^{1/2} \times 3^{1/2} \) vacancy superlattice is an ideal matrix for doping with metals. The capture of metal atoms during crystallization stabilizes additionally linear carbon chains in the solid state. Finally, a polycrystalline mosaic structure of carbyne macrocrystals is proposed that can explain the textured (spotted) diffraction pattern of hexagonal type observed experimentally.

1. Structural Investigations of Linear Carbon Matrix

Undoubtedly, the basis for recognition of any allotropic form is the individuality of its structure. Therefore, structural investigations play a particularly important role in studies of the elusive, to some extent ‘mysterious’ form of carbon - carbyne. Strictly speaking, it was the diffraction pattern, which does not belong to any other known carbon structure, that has initiated numerous investigations and controversies lasting already more than 30 years. Unfortunately, only small particles of several microns in size were reported to be available in the vast majority of studies as impurities in well crystallized (diamond and graphite) and amorphous carbon phases. Evidently, the mechanical isolation of the new substance in its pure state was very difficult in those cases. Furthermore, the insolubility and nonvolatility of the substance did not allow its isolation by chemical methods in amounts that would be sufficient to study all its properties. Thus, it is just this ‘adverse’ chemical nature of carbyne that is responsible for the unprecedented case, that a substance observed in dozens of independent scientific studies and synthesized by several totally different methods still has not been worldwide recognized by the scientific community. Consequently, owing to the lack of rigorous and reliable structural data a number of hypothetical models often based on the subjective opinion of the authors were published. These facts suggest that the ‘mystery’ of carbyne requires one additional careful, objective, and detailed review of all what has been done to date.

The term "carbyne" was introduced into the literature in 1961 by Russian researchers [1-3]. The simple but quite attractive idea concerning the existence of a carbon form constituted of \( sp \)-hybridized carbon atoms (along with \( sp^3 \) and \( sp^2 \) carbon allotropes, \textit{i.e.} diamond and graphite) provided a cornerstone for their research. The suffix "yne" used in organic chemistry to designate acetylene derivatives, had to reflect, according to the authors' intention, the \( sp \)-nature of the substance. Unfortunately, later the IUPAC adopted this term to refer to carbon-centered triradicals, used in particular for synthesizing \textit{polycarbynes} - crimped \( sp^3 \) carbon networks stabilized by phenyl groups [4,5]. The use of the term \textit{carbyne} thus requires some caution. For example, it is necessary to emphasize that \textit{polycarbyne} has nothing to do with one-dimensional carbon since it is a totally different substance.

In the first attempts, polycondensation reactions widely used to synthesize organic polymers were chosen to obtain carbyne. It was supposed that the sequence of chemical transformations would determine the nature of the linear structure of carbon expected to form. However, the polymeric nature of this material along with the extreme reactivity of unsaturated carbon fragments does not preclude the participation of other atoms and functional groups, present in the chemical reactor, in the formation of interchain cross-links and generally branched structures. The low-pressure thermolysis at 1000 °C could lead not only to removal of solvent molecules, but also could cause profound structural transformations in the entire sample. Thus, the mechanism and, therefore, the linear structure might not necessarily follow from the sequence of chemical reactions considered in those studies [6,7]. In particular, this remark concerns two possible electronic structures of polymeric molecules, \textit{viz.}, polyene and polycumulene types of the \( sp \)-bond symmetry. Nevertheless, the authors did manage to isolate pure (according to chemical analysis data) phase of gray carbon, using selective oxidation of black amorphous particles. It is just these structural data reported by Kasatochkin \textit{et al.} [8,9] that should establish a priority in the extending number of discoveries in this field. According to electron diffraction data, two types of crystals were observed with rhombohedral\(^1\) parameters \( a = 508 \) pm, \( c = 780 \) pm and \( a = 476 \) pm, \( c = 258 \) pm, called \( \alpha \)- and \( \beta \)-carbyne, respectively. It was supposed, that the former phase was less dense and might transform into the latter phase under thermobaric treatment [10]. The use of electron microscopy instead of usual x-ray diffraction method allowed to separate these phases, thus showing for the first time that the new carbon form can exist in at least two modifications.

This fact was not taken into account in studies of natural carbyne (according to the authors' term - Ries crater carbon [11]). Some 22 lines of a new substance in addition to 12 strong lines of graphite were present in the x-ray diffraction pattern. Simple mathematical treatment of the interplanar distance values on the assumption that all reflections belonged to one single phase gave the hexagonal parameters \( a = 897 \) pm and \( c = 1240 \) pm. Nevertheless, even in that case some lines, including a very strong line \( (d = 412 \) pm), probably corresponding to the \( (100) \) reflection of \( \beta \)-carbyne [12], were outside the experimental error.

Whittaker \textit{et al.} [13-16] observed carbyne in the carbon soot produced by sublimating graphite in vacuum. The variability of parameter \( c \) and relatively

\(^1\) To convert this to hexagonal parameters the value of \( a \) has to be multiplied by \( 3^{1/2} \).