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The Structural Chemistry of Crystalline Carbon: Geometry, Stability, and Electronic Spectrum

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The crystalline modifications of carbon described in the literature are briefly reviewed. The publications in which new types of structures, differing from the diamond and graphite lattices, are proposed and discussed are analysed in detail. The geometrical-topological characteristics of the hypothetical modifications of carbon, their relative stabilities, the nature of the chemical bonds, and the structure of the electronic spectra are discussed.
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I. INTRODUCTION

The carbon atoms forming part of the composition of hydrocarbon molecules stable under normal conditions can form chemical bonds with two, three, or four neighbours. As a rule in the first case the carbon atom and two of its partners are located on a single straight line, in the second case they form a planar molecular fragment with valence angles close to 120°, and in the third case a nearly tetrahedral disposition of the bonds is achieved. These features can be described in terms of the hybridisation theory, according to which carbon atoms tend to form directed two-centre σ-bonds with participation of sp-, sp^2-, and sp^3-hybrid orbitals; in the first two cases there is a possibility that additional bonds of the π-type may arise.

The numerous structural data for saturated and unsaturated hydrocarbons can be interpreted fairly reliably within the framework of the terms described above. Extended molecular systems in which carbon–carbon bonds are formed preferentially are of special interest. In the limit such systems can be regarded as infinite and consisting of carbon atoms only and can be divided into two groups: (1) systems made up of carbon atoms or small clusters of the latter having a regular structure in which the positions of the atoms or the clusters can be random; (2) systems in which the atoms are distributed regularly in three dimensions and form a complex bonded system with translational invariance. For example, carbon black, vitreous carbon, and various amorphous carbon films belong to the first, non-crystalline type, while crystals such as those of diamonds (cubic and hexagonal) and graphite (hexagonal and rhombohedral) belong to the second type.

Diamond and graphite are examples of extended systems in each of which sp^3 and sp^2 hybridisation obtains respectively; sp hybridisation arises in carbyne, which consists of linear macromolecules according to the investigators[1,2] who discovered this new allotropic form of carbon.

Together with diamond and graphite, whose structures have been thoroughly investigated, several other crystalline modifications of carbon have been described in the literature: up to eight carbyne forms, metallic carbon, C_8 carbon, etc., whose structures have not so far been established or have not been demonstrated sufficiently reliably.[3–6] The hypothesis has been put forward[7] that certain metastable carbon phases of unknown structure can arise in the growth of carbon layers on various crystalline modifications of boron nitride.

The modelling of the structure of amorphous carbon is an extremely complex problem and is extremely important for the interpretation of the physicochemical properties of the substance and for the creation of carbon materials with specified properties. In setting up a model of amorphous carbon, one usually employs the structural fragments of known crystalline modifications of carbon. For example, a model has been proposed[8] for the interpretation of the structure of sputtered amorphous carbon films according to which the structure of such a film can be represented as a bonded formation consisting of fragments of diamond-like and graphite-like types. The deficiencies of this model have been noted[9] and it has been emphasised that the earlier investigation[8] did not take into account the possibility of the formation of non-diamond-like and non-graphite-like fragments. Apparently the unsuitability of this model for the description of the structure of low-density carbon films is associated with this factor. The data quoted[9] also show that the most probable interatomic distance in the specimens obtained is intermediate between the lengths of single and double bonds; furthermore, the presence of multiple bonds is emphasised. A detailed analysis of experimental studies and model ideas used at the present time for the description of the structure of polymeric carbon has been carried out in a review.[10]

The existence of crystalline modifications of carbon of unknown structure, the difficulties arising in the modelling of the structure of amorphous carbon, and also the search for new carbon materials with a specified set of properties have led to the formulation of several theoretical problems which we believe to be extremely acute for the physical chemistry of carbon. It is necessary to discover whether the entire family of crystalline modifications of carbon is exhausted by the three forms described above—diamond, graphite, and carbyne, and, if not, what are the possible structures of these other hypothetical forms of carbon. It is also necessary to consider what evidence can be adduced in support of the possibility of the existence of such forms and what could be the physicochemical properties of these systems. This paper has been devoted to the analysis of the present state of these problems, which have been hardly discussed in the review mentioned above.[10]

II. CRYSTALLINE MODIFICATIONS OF CARBON DESCRIBED IN THE LITERATURE

There are two polytypical modifications of diamond: cubic diamond (D_c), which belongs to the $Fd3m$ symmetry space group and whose unit cell contains eight carbon atoms, and hexagonal diamond (D_h)—lonsdaleite, which belongs to the $P6_3/mmc$ symmetry space group and whose unit cell contains four carbon atoms.[11,12] The physical properties (density, hardness, electrical resistivity, and optical properties) of D_c and D_h are very similar, which is due to the identity of the first layer around each carbon atom in these diamond modifications; the valence angles are 109°28′16″ in both, the bond lengths are close to 1.545 Å, and the coordination number of each carbon atom is four. The difference between the second layers surrounding the carbon atoms in cubic diamond and in lonsdaleite is due to the fact that in cubic diamond all the layers made up of coordination tetrahedra are oriented in the same manner, while in lonsdaleite each succeeding tetrahedral layer is rotated by 60° relative to the previous layer.[13] Fragments of the crystal structures of D_c and D_h are presented, for example, in a monograph.[12]

The cubic modification of diamond is thermodynamically stable, being more stable than graphite at sufficiently high pressures, but it also exists at low pressures in a metastable state. The transformation of diamond into graphite takes place with a change in the first coordination sphere and in the type of chemical bond, which is the reason for the high energy barrier to the transformation and the low rate of the process. Lonsdaleite is a metastable modification of carbon; at high pressures it is transformed into cubic diamond and at low pressures into graphite. The phase transformations in carbon have been described in detail.[11,14]

Each carbon atom in diamond forms four stable covalent bonds with neighbouring carbon atoms and all the bonds are equivalent. The equivalence of the bonds in diamond makes it possible to employ the approximation of equivalent orbitals in the calculation of its band structure. The equivalent orbitals are linear combinations of atomic wave functions which are interconverted under the influence of the operations of the symmetry group of the crystal; this reduces the number of independent matrix elements and makes it possible to obtain the dependence of the energy of the molecular orbitals on the wave vector along symmetrical directions in the inverse space in an analytical form. The methods for the calculation of the electronic structure of crystals with the diamond structure have been considered in detail in a monograph.[15] The applicability of the method of equivalent orbitals to the description of the band structure of diamond indicates the localised character of the bonds in diamond, since the method of equivalent orbitals is particularly successful in a description of structures with localised bonds.

The second allotropic modification of carbon is graphite, which also exists in the form of two polytypic forms: hexagonal graphite (G_h) with a $P6_3/mmc$ symmetry group and four carbon atoms in the unit cell and rhombohedral graphite (G_r) which has a $R\bar{3}m$ symmetry space group and six carbon atoms in the unit cell.[11,12] Graphite has a layer structure and consists of hexagonal carbon layers linked by van der Waals forces. The structures of the layers in G_h and G_r are almost identical (the coordination number of carbon is three, the bond lengths are close to 1.42 Å, and the valence angles are 120°). However, the arrangements of the layers in these two modifications are different, which also leads to a difference between their crystal structures.[11,16] In hexagonal graphite each third layer repeats the first and each second layer is displaced relative to the first in such a way that half the atoms of each layer are located respectively above and below the centres of the hexagons of the neighbouring layers. The sequence of identical layers in G_h can be represented conventionally by the symbol ...ABABAB.... In rhombohedral graphite each fourth layer repeats the first. The sequence of the layers in G_r can be represented by the symbol ...ABCABC.... In several processes rhombohedral graphite always occurs in specimens of natural origin and in the products of the mechanical treatment of graphite.[16] The high degree of anisotropy of the physical properties of graphite (electrical conductivity and optical and thermal properties) is associated with the fact that the interaction between the hexagonal layers in graphite is much weaker than the interaction within each layer (the distance between the graphite layer is 3.35 Å); the physical properties of G_h and G_r are similar.

Of the four valence electrons of each carbon atom in graphite, three are involved in the formation of localised σ-bonds with neighbouring atoms. The fourth valence electron is located in the $2p$ orbital whose symmetry axis is at right angles to the plane of the hexagonal layer and participates in the formation of bonds of the π-type, which make up an extended delocalised π-electron system. The orthogonality of the orbitals of the electrons in the σ- and π-systems makes it possible to obtain the principal qualitative characteristics of the bands in the spectra of graphite in terms of the π-electron approximation, where only one $2p$ electron of each atom is taken into account and it is assumed that these mobile π-electrons migrate in the field of a rigid σ-skeleton.

Since the interaction between the layers of graphite, which is of the van der Waals type, is fairly weak, a two-dimensional model is frequently employed in the calculation of the band structure of graphite. The two-dimensional model leads to a zero width of the energy gap between the valence and conductivity bands and to a marked anisotropy of the properties of graphite, which agrees with experiment and the results obtained for the three-dimensional model. In order to achieve a quantitative agreement between theory and experiment, it is necessary to take into account also the interlayer interaction. The properties of graphite have been described by Ubbelohde and Lewis[16] and the methods for the calculation of its band structure have been described, for example, by Slonczewski and Weiss[17] and Ovchinnikov and Belyi.[18]

The principal properties of graphite and diamond have so far been adequately described in theoretical terms and the main efforts in this field are therefore nowadays directed to the study of diamond-like and graphite-like systems with less perfect and more indefinite structures (the influence of defects, the formation of layer compounds of graphite with various metals, the description of the band structure and properties of non-graphitised carbon, etc.), as well as the interconversions of the modifications of carbon and the conditions governing their formation.[11,16,19,20] Furthermore, diamond and graphite can be regarded as model systems on which it is possible to test various new methods and approximations of solid state physics and quantum chemistry.

As mentioned above, apart from diamond and graphite, there exist also other crystalline modifications of carbon whose structure is so far unknown or has been studied with inadequate reliability. In 1979 the synthesis of new cubic modifications of carbon with the $Im3$ symmetry space group and containing sixteen carbon atoms in the unit cell was reported.[5] The new crystalline modification of carbon, called by the authors C_8, was obtained by condensing fluxes of carbon plasma on cooled supports; C_8 is formed in the form of single crystal inclusions, whose size is up

to 3000 Å, in a carbon film. The theoretical density of the new modification $\rho = 4.1$ g cm^{-3}, i.e. is greater than the density of diamond (3.51 g cm^{-3}); the microhardness of C_8 exceeds that of diamond, the coordination number is 4, and the period of the body-centred lattice is 4.28 Å. This modification of carbon consists of coordination tetrahedra[21] of the same kind as in D_c and D_h but somewhat deformed and more closely packed. The valence angles in the C_8 modification differ from the tetrahedral values (90° and 125°16′), while the bond lengths are also different and greatly reduced (1.42 and 1.23 Å).

The structure of C_8 can be represented as a result of the polycondensation of cubane C_8H_8,[22] in which hydrogen is competely removed and the vertices of the carbon cubes are linked by chemical bonds. The bond lengths between the vertices of individual cubes are 1.23 Å, which is close to the lengths of the triple bond in acetylene; however, the C–C bond length in cubane is 1.55 Å.[23] The combination of a coordination number of 4 and bond lengths of 1.42 and 1.23 Å in C_8 is not altogether usual and conflicts with the empirical rules established for bond lengths in molecules,[24] according to which bond lengths of approximately 1.54 Å are characteristic of a carbon atom forming four bonds. Certain diffraction lines in the X-ray diffraction patterns, close to those found[5] for C_8, have been observed for the carbon particles obtained as a result of the exposure of octane, decane, and iso-octane drops to a laser beam.[25] Nevertheless the deviation of the bond length in C_8 from the classical values shows that the crystal structure of C_8 requires additional experimental confirmation.

The report[6] of the preparation (as a result of the impact compression of a graphite single crystal up to pressures in excess of 150 kbar) of a modification of carbon, which is metastable at atmospheric pressure and which has a cubic lattice with a period of 5.545 Å and 24 atoms in the unit cell, has also not been finally confirmed. The individual interplanar spacings, determined in the above study,[6] are encountered in carbon powders obtained on crystallisation of carbon from the gas phase and also in the same powders subjected to high pressures and temperatures corresponding to the region of stability of diamond.[26] The symmetry space group of this modification has not been established. The authors[6] merely quote a set of space groups compatible with the observed diffraction lines. The density of the modification is 2.8 g cm^{-3}, i.e. is intermediate between the densities of diamond and graphite (2.265 g cm^{-3}).[16]

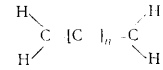
The phase diagram of carbon, in which a region of the thermodynamic stability of solid metallic carbon (carbon III) had been noted at high pressures ($p > 600$ kbar), was published in 1963.[27] The preparation of metallic carbon has been reported in another study,[4] but its structure had not been determined. The present ideas concerning the phase diagram of carbon have been described in detail by Bundy.[28]

Apart from the communications enumerated above concerning new crystalline modifications of carbon, there have been numerous studies devoted to crystalline modifications of carbon of the carbyne type. Up to eight modifications of carbyne are now known[3] (α-carbyne, β-carbyne, etc.), but the crystal structures of none of them have so far been established.

According to some investigations,[1–3,29,30] carbyne is a crystalline modification of carbon consisting of fairly long (number of carbon atoms approximately 10^3) linear carbon chains weakly interacting with one another. In the ideal case, there is a possibility of two carbyne forms, which can be described by the classical structural formulae

$$\sim\!=\!C\!=\!C\!=\!C\!=\!C\!=\!\sim$$
$$\sim\!-\!C\equiv\!C\!-\!C\equiv\!C\!-\!\sim$$

The end groups are not represented in these systems, although in fact such groups are extremely important for the understanding of the structural differences between these compounds. In the first case the macromolecule has the form



(I)

and is of the cumulene type. In the second case the macromolecule is of the poly-yne type:

$$H\!-\!\left[-C\equiv\!C-\right]_n\!-\!H\ . \qquad \text{(II)}$$

In the case of purely carbon macromolecules, a structure of an intermediate type should obtain.

Raman spectroscopic data[31] indicate the presence in the spectrum of the mineral chaoite[32] of a band at 2140 cm^{-1} corresponding to the stretching vibrations of the triple bond $-C\equiv C-$; however, this fact alone is insufficient to conclude that the molecules of chaoite let alone those of all the carbyne modifications of carbon are linear. Henceforth carbyne will be understood as a modification of carbon with a linear structure of its constituent macromolecules and as crystalline modifications of carbon whose structure has not been established and which have been classified as carbyne forms of carbon; however, in the future it may turn out that certain carbyne modifications of carbon known at present do not consist of linear molecules. The proposed agreement concerning terminology is justified by the fact that the term "carbyne" has penetrated the literature extensively and is used both in relation to model systems consisting of linear carbon macromolecules[33–36] and in relation to crystalline modifications of carbon whose structure has not been established with adequate reliability or is unknown.[1–3,25,26,29,37,38]

The methods used to prepare carbyne are extremely varied: synthesis from acetylene;[30,39] deposition of carbon vapour, obtained on sublimation of graphite by a laser beam, onto a glass or other support;[40] the formation of a white film of carbyne when an electric current is passed through a graphite rod;[41] plasma-chemical methods;[42,43] etc.[44,45] Unfortunately a single crystal of carbyne sufficiently large for the elucidation of its crystal structure cannot be obtained by any of these methods. Single crystals of carbyne (chaoite), discovered in a meteorite crater,[32] in natural graphite deposits,[37] and in a meteorite[46] are also too small to determine their crystal structure.

The data obtained in the study of carbyne modifications of carbon lead to the following ideas about its structure and properties. Carbyne is a white substance[32,37,41,47] with an almost 100% content of carbon, whose density is intermediate between those of diamond and graphite, and which is chemically resistant to oxidants and other reagents.[48] Carbyne single crystals with dimensions up to 10^4 Å have hexagonal symmetry[1,2,32,38] and the unit cell contains a large number of carbon atoms (for example 144 for α-carbyne and 72 for β-carbyne[1,29]), which hinders the determination of its crystal structure from diffraction data. According to Whittaker,[3] the region of thermodynamic stability of carbynes is at temperatures from 2600 to 3800 K. On heating (by an electric current in an atmosphere of argon), graphite is slowly converted into linear forms of carbon, the reverse process occurring rapidly on cooling.[49] At pressures greater than 60 kbar, the carbyne forms of carbon are converted into diamond-like structures and, on reducing the pressure to 0 2 atm and less, carbyne sublimes.

According to some data,[26,50,51] the β-modification of carbyne is more stable at high pressures, while the α-modification is more stable at lower pressures. Some

data on the heat capacity of carbyne[52] indicate the quasi-one-dimensionality of its molecules but at the same time there have been reports[1,54] that, as a consequence of the high reactivity of the carbon chains, it is very difficult to avoid the formation of chemical bonds between them (with increase of their length) during the preparation of carbyne chemically. It may be that, as a consequence of this, in the synthesis of carbyne the final product always contains a definite number of bonds between the chains whose positions cannot be determined by X-ray and electron diffraction.

Overall, the available information about the physical properties of carbyne is fairly scanty, which leads to arbitrary theoretical constructions and estimates concerning carbyne, since the present state of the methods for the calculation of the electronic and crystal structures of solids precludes a reliable prediction of any one property of the solid without resorting to experimental data. At the same time, it is essential to note that most investigators have no doubt about the existence of crystalline modifications of carbon of the carbyne type because X-ray and electron diffraction methods lead to structural parameters of carbyne which are definitely different from those of diamond and graphite.[1,29,47,54,56] Furthermore, photoelectron spectroscopic data[55] also indicate significant differences between the spectra of diamond, graphite, and carbyne. Apparently carbyne has a characteristic ionic spectrum (the ratio of the concentrations of the C_2^- and C_6^- ions),[49,57] which makes it possible to employ ionic spectrometry for the detection of microinclusions of carbyne in carbon specimens of natural and artificial origins.

We may note that, in the literature devoted to theoretical studies of the electronic structure of carbyne, for example, in the communication of Misurkin and Ovchinnikov,[58] the activation energy for electrical conduction in carbyne, obtained from the measurement of the temperature variation of the electrical conductivity, is quoted as $\Delta E = 1-2$ eV and this value is identified with the width of the forbidden gap in carbyne $\Delta\varepsilon$. However, in another investigation[59] the conductimetric measurements were performed on a specimen consisting of a black insoluble powder containing 98% of carbon and obtained by the polycondensation of acetylene. At the same time it is known that in other methods of synthesis the carbyne forms of carbon are white and contain almost 100% of carbon. The activation energy for electrical conduction in the black specimen must have been influenced by admixtures and the boundaries between the grains, so that these data[59] concerning ΔE can hardly be correctly attributed to carbyne forms of carbon. The white colour of the carbon films is more probably an indication that the width of the forbidden gap in the electronic spectrum of carbyne is greater than the maximum energy of the photon in the optical range, which is 3.3 eV.

The carbyne macromolecules have been investigated by various quantum-chemical methods: in the π-electron approximation, in the valence approximation, and taking into account all the electrons. Special interest in this branch of the quantum chemistry of polymers arose in the second half of the 1960's [30] when it was suggested that carbyne consists of linear carbon chains or of fairly long hydrocarbon molecules of types I and II. The real differences between systems I and II are manifested primarily in the geometry, which in the case of system (I) depends on the parity of the number n. The carbon skeletons of the molecules of (I) and (II) are linear. In the former case the C–C bond lengths are identical and close to 1.3 Å, while in the latter case they alternate and the extent of this alternation apparently depends little on n. The electronic spectra of systems (I) and (II) are also different. The energy of the first transition for the molecule of the cumulene type tends to zero, while in the case of the poly-yne system there is a forbidden gap whose width is non-zero.[60–63] For small values of n, the influence of the end groups on the C–C bond length is extremely significant. Calculations for a series of compounds C_4, C_4H_2, C_4H_4 and C_6, C_6H_2, C_6H_4 have been carried out[64] in terms of the valence approximation by the extended Hückel method (EHM) using Cusachs' parametrisation[65] with partial optimisation of the geometry; in the case of the C_4H_2, C_4H_4, and C_6H_2 molecules the calculations led to results close to the experimental data. Qualitative estimates of the C–C bond length in the linear C_4 and C_6 molecules have been made on the basis of these calculations.

Results indicating an appreciable influence of the end effects on the geometrical characteristics of the inner parts of the molecules of the given type, containing a fairly large number of carbon atoms, have been obtained.[66] The same communication[66] presents results of quantum-chemical calculations for molecules of the types C_nH_2, C_nH_4, and C_n (linear configuration) with $n \leq 18$ in the valence approximation of the EHM. A model was used in which it was assumed that the distance r between the carbon atoms is related to the corresponding bond population (Mulliken population) p by the expression

$$r = 1.860297 - 0.54869p + 0.109747p^2$$

found on the basis of calculated data for acetylene, benzene, ethylene, and ethane.

The calculation in the above study[66] was iterative. Hoffmann[66] analysed in detail the disadvantages of this model and noted in particular that the agreement in terms of the bond orders may not correspond to the total energy minimum. However, the bond lengths found for a small value of n proved to be close to the experimental lengths (allene, butatriene, diacetylene, triacetylene) and this factor served to some extent as justification of the possibility of employing this approach for high values of n. The results of Hoffmann's calculations[66] led to the conclusion that the influence of the end groups on the bond lengths in the C_n, C_nH_2, and C_nH_4 molecules is extremely significant, at any rate for $n < 20$.

In order to solve the question of the possible existence of fairly long molecules of the type C_nH_2, C_nH_4, and C_n, a whole series of quantum-chemical calculations were performed for model linear systems of the C_n type consisting of a large number of carbon atoms. These calculations were performed in terms of different approximations: at the π-electron level taking into account the influence of the σ-skeleton by an additive scheme, taking into account all the valence electrons (EHM, CNDO/2, and the method of a three-dimensional electron gas), and by non-empirical methods.[34–36,67–73] In some of these studies[67–72] Bloch's cyclic model was used. The possibility of the alternation of the lengths of neighbouring C–C bonds (r_1 and r_2) was assumed. The average total energy per elementary fragment (in the given case the elementary fragment consists of two carbon atoms) was regarded as a function of two independent parameters and was optimised. All these calculations led to the same qualitative conclusions regardless of the approximation employed: the minimum average potential energy of the $^\sim C_n$ system in the limit at $n \to \infty$ is reached when $r_1 \neq r_2$ and the C_∞ system is stable in relation to dissociation into diatomic fragments.

On the one hand, the conclusion of the alternation of the bond lengths is satisfactorily consistent with the Peierls theorem, which states that one-dimensional systems with

an energy spectrum of the metallic type are unstable, since the alternation of the bond lengths automatically leads to the appearance of a gap in the spectrum, which is manifested even in the Hückel π-electron approximation. On the other hand, it has been shown in a number of studies that, in terms of the π-electron approximation, when account is taken of the correlation effects, the width of the gap is not zero also when the bond lengths are equal ($r_1 = r_2$, see, for example, the relevant reviews[58,74]). It has been concluded[58] that in cumulene chains with a sufficiently large number of carbon atoms an antiferromagnetic state obtains and for this reason the bond lengths may be identical in long cumulene molecules far from the ends. However, we may note that this conclusion has been reached in terms of the π-electron approximation.

In conclusion one should note that, from our point of view, the use of the average value of the total energy for the estimation of the local geometrical properties of the molecule is an unduly rough approximation: the model leads *a priori* to an average bond length and for this reason the average total energies of the C_n, C_nH_2, and C_nH_4 systems with the same geometry of the carbon skeleton tend to the same limit and caution must be exercised in interpreting the results obtained within the framework of this model However, the conclusions reached in a number of studies[67-72] do not conflict with the possibility of the existence of fairly long molecules of the type C_n, C_nH_2, and C_nH_4. At the same time, the high reactivity of such systems can lead to the presence of intermolecular cross-links and, in order to avoid them, it is necessary to isolate the molecules from one another in some way. One of such procedures, associated with the synthesis of carbyne forms of carbon from tetrafluoroethylene, has been discussed.[75]

III. HYPOTHETICAL CRYSTALLINE MODIFICATIONS OF CARBON

1. The Geometrical-Topological Properties of Crystalline Carbon and Certain Energy Estimates

Diamond and graphite are two allotropic crystalline modifications of carbon which differ from one another both in the type of structure and in the coordination numbers of the atoms.[12] The structures of diamond and graphite are free from strain, since their valence angles agree with the classical angles for tetracoordinate and tricoordinate carbon atoms respectively. All the bonds in diamond are equivalent and the carbon atoms are located in structurally equivalent positions. To within fairly weak interlayer interactions, the positions of the atoms in graphite are also equivalent; the bonds in the graphite layer are equivalent to one another also when account is taken of the interlayer interactions. The characteristic features of the diamond and graphite structures enumerated above (the equivalence of the bonds and of the positions of the atoms, the absence of strain) distinguish them from the multiplicity of the remaining modifications of carbon listed above; apparently these features are responsible for the stability of diamond and graphite and their wide occurrence in nature.

If the macromolecules of carbyne have a linear structure, then its valence angles should be 180°, which also leads to the absence of strain, because an angle of 180° is characteristic of the dicoordinate carbon atom. In a structure of the cumulene type, the C–C bonds are equivalent and all the atoms occupy equivalent positions, provided that, as in graphite, one neglects their intermolecular interaction. In a structure of the poly-yne type, the equivalence of the bonds breaks down, but a linear chain of the poly-yne type is also free of strain. The deviations of the structural type of carbyne and of the coordination number of atoms in it from the corresponding characteristics of diamond and graphite make it possible to regard carbyne as the third allotropic crystalline modification of carbon.

We shall now consider the question whether there is a possibility of further crystalline modifications of carbons free from strain. Such a possibility will be considered in a purely geometrical sense and the identity of the valence angles with the classical values (109°28′16″, 120°, and 180° for tetracoordinate, tricoordinate, and dicoordinate carbon atoms respectively) will be regarded by convention as the criterion of the absence of strain.

The presence of chemical bonds between the carbon atoms in diamond and graphite makes it possible to describe naturally the structures of these compounds in terms of regular networks. The term "net" is used in this review as a non-oriented graph with an infinite number of vertices located in a three-dimensional space at the points corresponding to the positions of the lattice atoms. The vertices are assumed to be adjacent when the interatomic distances do not exceed 1.6 Å. In diamond the corresponding graph is connected and homogeneous and the degree of each of its vertices is 4. In graphite the graph is subdivided into an infinite number of subgraphs corresponding to individual layers. Carbyne can also be described in terms of an infinite number of subgraphs, each subgraph being linear. From the standpoint of the graph theory, the positions of the vertices and the lengths of the edges as well as their form are not significant. The problem of describing the possible crystalline modifications of carbon (CMC) is therefore a special case of the problem of describing infinite graphs satisfying the following properties: a graph must permit a geometrical construction in which the angles between the edges (in the given instance we consider the sections connecting the vertices) are identical with or close to the classical valence angles in the C–C bonds. Furthermore, the geometrical graph must have the property of periodicity and the number of atoms in the elementary fragment should not be very large.

Thus graph theory may be used for the description of structures which satisfy the essential requirements of valence theory for the carbon atom. We shall discuss initially the structures of the graphite-like type described by a system of unconnected graphs with a degree of 3, each of which can be represented in the plane as a periodic structure.

In connection with the problem of the existence of new crystalline modifications of carbon, this approach has already been used.[76] The authors of that investigation discussed mainly geometrical graphs with a mosaic structure made up of a combination of different carbon rings: four-membered and eight-membered, three-membered and twelve-membered, and also five-membered and seven-membered. Some of these planar systems are illustrated in Fig. 1. In all the structures there are extended π-electron systems. The valence angles deviate from 120°; the degree of each vertex of the graph is 3. For example, in the graph $(3:4,8^2)$ (Fig. 1*b*) two valence angles are 135° and the third is 90°. Here we have made use of a notation which is convenient for certain homogeneous graphs; the number 3 denotes the degree of the vertex and the numerals 4 and 8 represent the size of the rings to which each vertex belongs. In the graph $(3:4,8^2)$ each vertex belongs to one four-membered and two eight-membered rings, which is denoted

by the superscript 2 to the numeral 8. $(3:6^3)$ corresponds to a graphite layer (Fig. 1*a*) in terms of the same notation. Fig. 1*c* represents also a (3:5,7) net made up of five- and seven-membered rings. The deviation of the valence angles in the $(3:4,8^2)$ net from 120° leads to an energy gain compared with graphite, where the valence angles are 120°, The energy of the steric strain (E_{SS}) has been estimated[76] from the empirical formula $E_{SS} = 17.5\Delta\theta^2$ cal mol^{-1}, where $\Delta\theta$ is the deviation of the valence angles from the ideal value (120° or 109°28′16″ in the case of sp^2- or sp^3-hybridisation respectively). In estimating the relative stabilities of planar nets, account was also taken of the conjugation energy (E_{conj}) calculated in terms of the Hückel approximation.

Among the three-dimensional nets considered by Balaban et al.,[76] the net whose fragment is illustrated in Fig. 1*e* is of greatest interest. It is described in terms of truncated octahedra and the valence angles (90° and 120°) differ fairly appreciably from the tetrahedral values (the steric strain energy is 12 kcal mol^{-1}). The relative stability of this system was determined in relation to diamond (cubic) and the relative stabilities of graphite and diamond were estimated from the difference between the enthalpies of formation. The energies of the other (planar) forms shown in Fig. 1 were estimated in the way described above and were assumed to be $E_{SS} + E_{conj}$. This analysis resulted in the following stability series (in kcal mol^{-1}): graphite (0.0), cubic diamond (0.5), hexagonal diamond (3.0), system (*c*) (7.5), system (*e*) (12.0), and system (*b*) (17.0). A higher energy corresponds to the other nets considered in the above study.[76]

It is seen from the above analysis that the estimates obtained[76] are extremely approximate. In particular, the authors[76] in essence restricted their treatment to a purely topological approximation and did not attempt to estimate the bond lengths in the carbon structures which they considered. Apparently, the assumption of the planar character of the systems and in particular of the net made up of four- and eight-membered rings is insufficiently justified. For example, it is known that the eight-membered carbon ring in cyclo-octatetraene and its octamethyl derivatives is non-planar; a doubt therefore arises about the reality of system (b) which can hardly be planar.

Planar regular nets are the limiting case of finite nets which can be produced on a sphere with a sufficiently large radius. In this case a convex polyhedron can be associated with each such net. The possibility of the existence and methods of synthesis of some of the hydrocarbon systems whose carbon atoms are located at the vertices of the simplest polyhedra (the cube, the trihedral prism, the tetrahedron, and the dodecahedron) has been discussed in a number of studies.[77–82]

The possibility of the occurrence of the analogous unsaturated purely carbon systems—molecules whose atoms are located at the vertices of polygons or polyhedra has been considered in a number of studies.[83–89] Certain results obtained for small carbon clusters, including planar clusters, are of interest in this connection. For example, the potential energy surface for the C_3 triatomic molecule has been investigated[83] by the non-empirical LCAO-MO method. It was established that a linear configuration is most stable

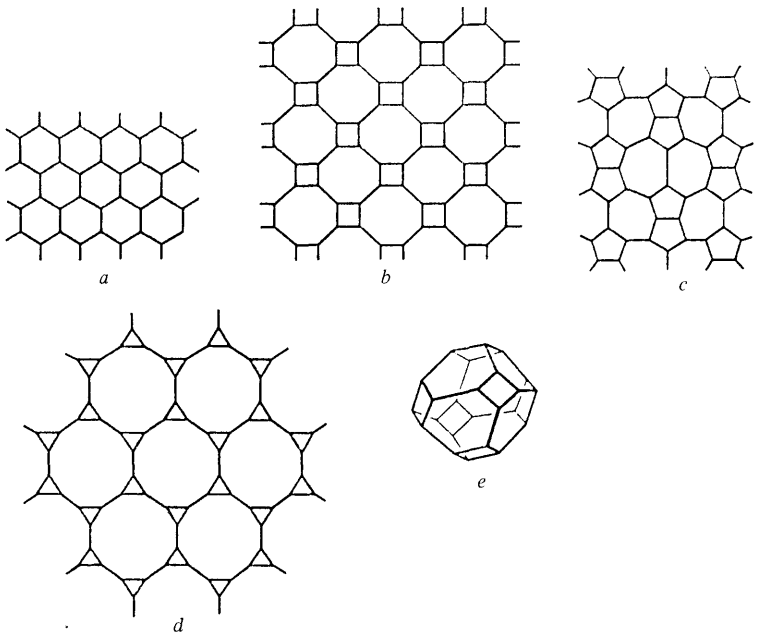


Figure 1. Some of the carbon systems considered by Balaban et al.[76]: *a*) $(3:6^3)$ graphite layer; *b*) $(3:4,8^2)$ system; *c*) (3:5,7) system; *d*) $(3:3,12^2)$ system; *e*) fragment of three-dimensional net.

for this molecule. Furthermore, a local minimum, corresponding to a trigonal configuration of the nuclei in the form of an isosceles triangle, was noted on the potential energy surface. The molecule has a triplet ground state.

A recent calculation for the C_4 cluster led to an unexpected result. It was found that the cyclic system in the form of a rhombus is energetically more favourable than the linear system.[84] The relative stabilities of various symmetrical configurations of clusters having the composition C_p ($p = 3-7$) have been discussed[85] within the framework of the semi-empirical MINDO/2 approximation. In particular, it was established that, for each of the C_3-C_7 clusters, there exist at least two isomers and that the absolute energy minimum corresponds to a non-linear configuration. For example, in the case of C_4 the most stable configuration is the rhombus (D_{2h} symmetry), which is consistent with the conclusions reached[84] by a non-empirical method. A distorted octahedral configuration obtains for C_6. In the case of C_4 a linear configuration proved to be unstable, but for other clusters (C_5, C_6 and C_7) local minima on the potential energy surface correspond to linear configurations. The relative stabilities of small carbon clusters have also been discussed by Beran et al.[86]

The electronic structures and relative stabilities of the carbopolyhedra with a large number of carbon atoms have been investigated.[87-89] The authors of these studies carried out calculations by various quantum-chemical methods for the carbododecahedron (C_{20}), the carbo-*s*-octahedron (C_{24}), which is a polyhedral fragment of the three-dimensional net (*e*) (Fig. 1), and carbo-*s*-eicosahedron (C_{60}) (Fig. 2).

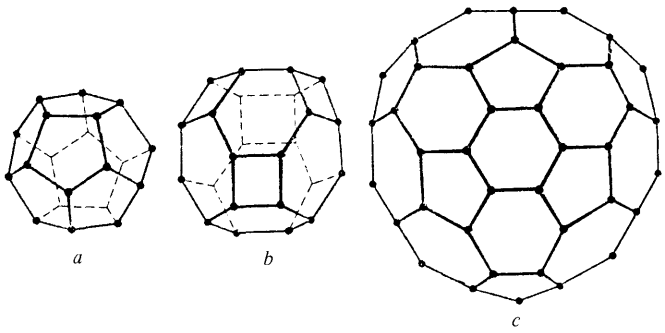


Figure 2. Carbopolyhedra: *a*) carbododecahedron; *b*) carbo-*s*-octahedron; *c*) carbo-*s*-eicosahedron.[87]

In the simplest case an approximation analogous to the Hückel approximation for planar unsaturated conjugated systems, which has been called[87-89] the ρ-approximation, was used. It was assumed that the σ-skeleton of the carbopolyhedra is made up of two-centre two-electron banana bonds in which the 2*s* and 2*p* orbitals of the carbon atoms participate. The remaining *p* orbitals are directed along the radius of the sphere described and the electrons associated with these orbitals are involved in the formation of the ρ-system on the sphere analogous to the π-system in the limiting case of the sphere—the plane.

The calculations performed in terms of the ρ-approximation[83] showed that the ρ-electron shell of the carbododecahedron is not closed (in the highest quadruply degenerate level there are two electrons), while the carbo-*s*-octahedron and the carbo-*s*-eicosahedron have a closed electron shell. The calculations performed with the aid of the EHM confirmed the conclusion concerning the character of the electron shells of the ground states of the carbododecahedron, the carbo-*s*-octahedron, and the carbo-*s*-eicosahedron. By varying the C–C bond lengths in C_{20}, C_{24}, and C_{60} while retaining the ideal symmetry for these systems, an equivalent value close to the length of a single bond was attained. In the case of the C_{20} system the above calculation shows that such a molecule, if it exists, should have the form of a distorted dodecahedron. Naturally, the symmetry of the carbododecahedron can be reduced by replacing two carbon atoms by boron atoms and by reducing thereby the total number of ρ-electrons by two. Such systems have a closed electron shell (EHM, ρ-approximation) and it is believed[87-89] that no obstacle to the possibility of their existence has so far been found.

The results described above have been confirmed by calculations carried out by the CNDO-2 method.[88,89]

We shall now proceed to the description of certain connected three-dimensional infinite regular nets, which can be achieved in three-dimensional space in such a way that the valence angles are equal to or close to the classical values. Apparently, one of the first studies on these lines[91] was published as early as 1946; its authors describe the structure of carbon made up of six-membered rings notated relative to one another. A net formed in three-dimensional space as a result of regular cross-links between the carbon skeletons of *o*-tetraphenylene, whose molecules are non-planar, corresponds to this crystalline modification of carbon. A net of this type has been used[91] to construct one of the possible models of amorphous carbon.

In relation to structural problems of crystal chemistry and crystallography, three-dimensional nets have been investigated systematically by Wells, who described a number of three-dimensional nets, suitable for the understanding of the topology of crystals with a complex structure, in a series of articles[92-103] about the geometrical principles of crystal chemistry, which were summarised in a monograph.[104]

In principle, any three-dimensional nets, including those with a regular structure, can be readily obtained with the aid of the operations involving the addition of new vertices or edges, for example, to a graph consisting of an infinite number of unconnected linear graphs. The problem consists in selecting those graphs which can be realised in the form satisfying the requirements formulated above.

A natural method of obtaining some of these nets (homogeneous graphs of degree 3), in which the valence angles, equal to 120°, are combined with a non-planar structure, has been described;[105,106] this is a type of coordination structure, as in diamond.

We may note that the planar layer of graphite can be regarded as a result of the formation of chemical bonds, i.e. regular cross links between zig-zag chains made up of carbon atoms located in a single plane. The valence angles are assumed to be 120° and each chain has two neighbouring chains. One can form analogously a chain made up of carbon atoms and having an *n*th order screw symmetry axis, in which the angles between the bonds along the chain are 120°, by distributing the carbon atoms along the edges of a regular straight *n*-hedral prism ($3 \leq n \leq 6$). Having arranged such prisms parallel to the *z* axis in such a way that each has *n* neighbours (Fig. 3), it is possible to form a system of cross links between the carbon chains which is periodic along the *z* axis. The periodic arrangement of the chains in space leads in this case to the formation of a crystal structure.

In fact, if it is assumed that the atomic orbitals are sp^2-hybridised, then the symmetry axis of the third hybrid orbital lies in a horizontal plane. Having arranged the set of chain macromolecules with parallel axes in space in a regular manner in such a way that in the direction of the horizontal hybrid atomic orbital (AO) of each atom there is an atom of a neighbouring chain (also having a hybrid atomic orbital directly at right angles to the z axis), it is possible to obtain a crystal structure in which each atom has three neighbours (two in its own chain and one in a neighbouring chain) and the valence angles are 120°. (When there is physical interaction between the atoms, there is a possibility of a distortion of the valence angles in certain structures.)

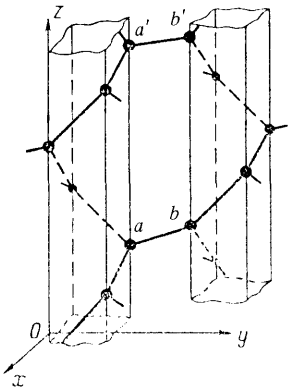


Figure 3. The principle of the construction of three-dimensional nets: the cross links between two adjacent chain systems having the 4_1 symmetry axis; the sections ab and $a'b'$ are parallel to the $z = 0$ plane.

Since fifth order [five-fold?] symmetry axes are impossible in crystals, it follows that $n \neq 5$. When $n = 6$, the chain degenerates into a planar regular hexagon and the cross-linking of such hexagons leads to the formation of a planar graphite layer. There remain two possible versions: with $n = 3$ and $n = 4$. When $n = 3$, the angles between the bonds along the chain are 120°, provided that the selected length of the side of the base of the trihedral prism is $r_1\sqrt{3}$ and the pitch of the helical chain (i.e. the difference between the z coordinates of the neighbouring atoms) is $r_1\sqrt{2/3}$, where r_1 is the distance between the neighbouring atoms along the chain. The distance r_2 between the nearest atoms of neighbouring chains is not related to r_1 and the choice of r_2 does not influence the symmetry of the crystal structure when $n = 3$. When $n = 4$, the valence angles are 120° when the side of the base of the tetrahedral prism and the pitch of the helical chain are $r_1\sqrt{2}$, where r_1 is also the distance between the neighbouring atoms along the chain.

Since the chains can have different chiralities, then for a given n there is a possibility of different versions of cross links leading to the formation of crystal structures. If the chiralities of the cross-linked chains are identical, then for a given n there is a possibility of only one method of cross-linking in which each chain with an nth order [n-fold?] screw symmetry axis is surrounded by n chains with the same chirality. The structures formed by the cross-linking of chain macromolecules of the same chirality will be designated by $C_1(n_j)$, where n_j characterises the screw symmetry axis of the chain macromolecule. The symbol $C_2(n)$ designates the crystalline carbon structures in which each chain with an nth order [n-fold?] screw symmetry axis is surrounded by n chains of the opposite chirality. In this case there is also a possibility of only one version of cross-linking. All the remaining structures formed by the cross-linking of chains of different chirality will be designated by the symbol $C_3^i(n)$, where i is an additional index. In structures of this type there are chains which have neighbours of different chirality.

Some of the other methods of cross-linking chain macromolecules described above, which lead to the formation of the $C_1(n_j)$, $C_2(n)$, and $C_3^i(n)$ structures, are shown in Fig. 4. Evidently it is possible to construct an infinite set of structures of the type $C_3^i(n)$; however, in modifications of this type the unit cells would contain too large a number of atoms.

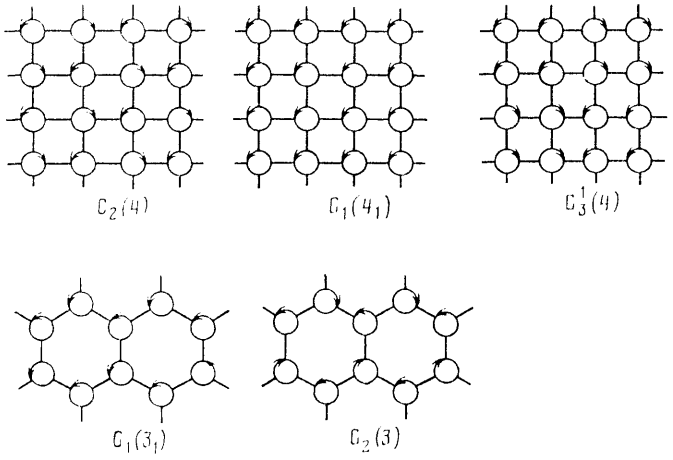


Figure 4. Classification of some of the three-dimensional crystalline modifications of carbon formed by cross links between chain macromolecules having symmetry screw axes of different orientations:[123] the orientations of the axes are indicated by arrows.

We shall consider in greater detail the crystal structures of certain modifications.

(a) *The $C_1(4_1)$ modification.* This modification is formed by the cross-linking of carbon chain molecules having 4_1 screw symmetry axes. Each of the chains has four neighbours of the same chirality. All the bonds are equivalent, so that one can assume that $r_1 = r_2 = r$. In the two directions perpendicular to one another and the 4_1 axis of each chain, there are helical chains of the same chirality as the initial chains.

The symmetry space group of the structure formed is $I4_132$ (see Bokii,[107] pp. 90, 104, No. 220). There is a body-centred cubic (BCC) Bravais lattice, in the unit cell there are eight carbon atoms, and the lattice parameter is $a = 2\sqrt{2}r$. The density of this modification ρ(g cm^{-3}) depends on the parameter r(Å) characterising the distance between the neighbouring carbon atoms: $\rho = 7.04/r^3$. For

example, $\rho = 2.46$ g cm^{-3} for $r = 1.42$ Å and $\rho = 1.93$ g cm^{-3} for $r = 1.54$ Å.

Each carbon atom in the $C_1(4_1)$ modification is located in one place with its neighbours, but the planes corresponding to sets of three terminal atoms in the C_6 fragments of the ethylene-like type intersect at an angle of 70°32′. By virtue of the total symmetry of the structure, when account is taken of the interaction between the atoms, significant distortions of the valence angles could not take place.

The enantiomorphic modification $C_1(4_3)$, formed by the cross-linking of chain carbon macromolecules having screw symmetry axes 4_3, has the $I4_332$ symmetry group. The scalar physical properties of the two enantiomers should be identical.

(b) *The $C_2(4)$ modification.* The structure of $C_2(4)$ and its projection on to the (001) plane are shown in Fig. 5. The $C_2(4)$ modification can be regarded as a result of the formation of regular cross links between chain carbon molecules having screw symmetry axes 4_1 and 4_3. Each chain has four neighbours of opposite chirality. All the valence angles can be chosen equal to 120°, provided that one disregards the possible distortions of the angles under the influence of interatomic interactions.

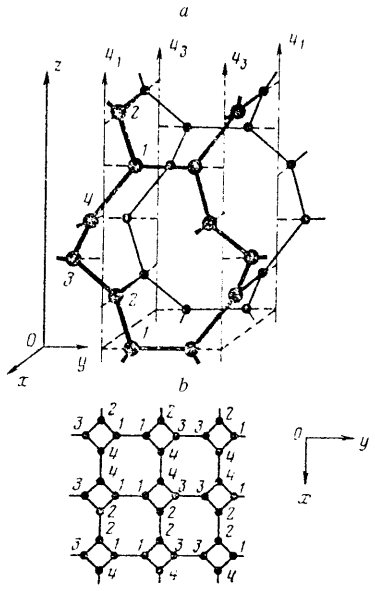


Figure 5. The crystal structure of the $C_2(4)$ modification:[112] *a*) structural fragment; *b*) view from above; identical numerals correspond to atoms whose *z* coordinates are equal or differ by amounts which are multiples of the period of translation along the *z* axis.

In contrast to the $C_1(4_1)$ modification, the bonds within the chain and between the chains are not equivalent. This is associated with the fact that the planes containing the carbon atom and the first layer around it are identical for the nearest atoms of neighbouring chains (the C_6 planar fragment), while non-planar C_6 fragments, with an angle of rotation of the corresponding planes of 70°32′ [the same as in $C_1(4_1)$], arise along the chain. The symmetry space group of this modification is $I\bar{4}m2$,[107] (pp. 80 and 96, No. 119). The Bravais lattice is hexagonal body-centred; the unit cell contains sixteen carbon atoms and the primitive cell contains eight carbon atoms. The unit cell parameters are $a = b = 2(r_1 + r_2)$ and $c = 2\sqrt{2}r_1$ The basis of the lattice consists of eight atoms; the volume of the unit cell is $v = 8\sqrt{2}r_1(r_1 + r_2)^2$. The density of this modification ρ depends on the two parameters r_1 and r_2: $\rho = 28.16/r_1 \cdot (r_1 + r_2)^2$. When $r_1 = 1.48$ Å and $r_2 = 1.34$ Å, we find $\rho = 2.39$ g cm^{-3}.

(c) *The $C_1(3)$ and $C_2(3)$ modifications.* The $C_1(3_1)$ modification and the enantiomorphic $C_1(3_2)$ modification have the symmetry space groups $P6_222$ and $P6_422$ respectively[107] (pp. 85 and 100, Nos. 183 and 184). The $C_1(3_1)$ modification, formed by the cross-linking of chain carbon macromolecules having symmetry screw axes 3_1, has a primitive hexagonal Bravais lattice containing six carbon atoms in the unit cell. The unit cell parameters are $\alpha = \beta = 90°$, $\gamma = 120°$, $a = b = (2r_1 + 3r_2)/\sqrt{3}$, and $c = r_1\sqrt{6}$, where r_1 is the distance between neighbouring atoms along the chains and r_2 is the distance between the nearest atoms in neighbouring chains.[106] The angles of rotation of the planes containing the atom and its immediate environment, corresponding to the transition to a neighbouring atom along the chain and to a neighbouring atom in a neighbouring chain, are 70°32′ and 38°56′ respectively. The density of the $C_1(3_1)$ modification with $r_1 = r_2 = r$ is defined by the expression $\rho = 6.76/r^3$; for $r = 1.48$ Å, we obtain $\rho = 2.08$ g cm^{-3}.

The $C_2(3)$ modification is made up by the cross-linking of chain carbon macromolecules having symmetry screw axes 3_1 or 3_2. Each chain has three neighbouring chains of opposite chirality. The Bravais chain is hexagonal and doubly body-centred, the unit cell contains eighteen carbon atoms, and the symmetry space group is $R\bar{3}m$,[107] (pp. 84 and 98, No. 166). The lattice parameters are $\alpha = \beta = 90°$, $\gamma = 120°$, $a = b = 2r_1 + 3r_2$, and $c = r_1\sqrt{6}$, where r_1 and r_2 have the same significance as for the $C_1(3_1)$ modification. The angles of rotation of the planes containing the atom and its first shell, corresponding to the transition from the atom to its neighbours along or between the chains, are 70°32′ and 0° respectively.

It is noteworthy that the projections of the structures described onto the (001) plane are of the same type as some of the planar carbon nets discussed[76] in connection with the assessment of the possibility of the existence of hypothetical planar carbon structures (Figs. 1 and 5).

We may also note that new crystal structures can be obtained from the crystalline modifications of carbon of the type $C_1(n_1)$, $C_2(n)$, and $C_3^i(n)$ by the formal replacement of the C–C bonds by the $-C\equiv C-$ fragments. Hybridisations of two kinds are formally obtained in crystalline modifications of carbon of this type: sp^2 and sp. According to Kasatochkin's classification,[53] these modifications refer to transitional forms of carbon.

As a result of the cross-linking of chain carbon macromolecules, it is possible to construct yet another homogeneous C_5 net. We shall consider a planar linear chain macromolecule consisting of an infinite number of carbon atoms and having the *trans*-configuration. Suppose that the lengths of all the bonds are identical and equal to r_1 and that all the valence angles are 120°. With the aid of the translational operation in a direction perpendicular to the molecular plane with a translation vector having a length $r_1\sqrt{3}$, we shall construct from the initial chain macromolecule an infinite family of its images, which are located in parallel equidistant planes. It follows from this method

of construction that the centres of all the bonds of the family of molecules obtained in this way are located in the same plane, which we shall designate by $\tilde{S}_0$. The set of all the macromolecules forms the layer S_0, consisting of chain macromolecules located in parallel planes and separated from one another by a distance $r_1\sqrt{3}$. We shall direct the z axis at right angles to the $\tilde{S}_0$ plane and the origin of coordinates will be placed in this plane. Then each atom of the $\tilde{S}_0$ layer has a z coordinate equal to either $r_1/4$ or $-r_1/4$.

We shall construct yet another layer S_1 of this kind. We shall rotate it relative to the initial layer by 90° and, having retained the previous orientation of the z axis, we shall place it above the S_0 layer at a distance r_2 in such a way that an atom of the S_1 layer with the z coordinate equal to $-r_1/4$ relative to the $\tilde{S}_1$ plane corresponds to each atom of the S_0 layer with a coordinate $r_1/4$ relative to the $\tilde{S}_0$ plane and both atoms are located on a single line perpendicular to the $\tilde{S}_0$ plane. It is easy to show that this procedure is feasible.

We construct analogously an S_{-1} layer and place it below the S_0 layer at a distance r_2. Continuing this process without limit, we obtain an infinite system of layers in which each even layer is rotated relative to the odd layer by 90° and an atom of the S_{n+1} layer with a relative z coordinate $-r_1/4$ corresponds to each atom in the S_n layer with a relative z coordinate $r_1/4$ and both atoms are located on a single straight line parallel to the z axis.

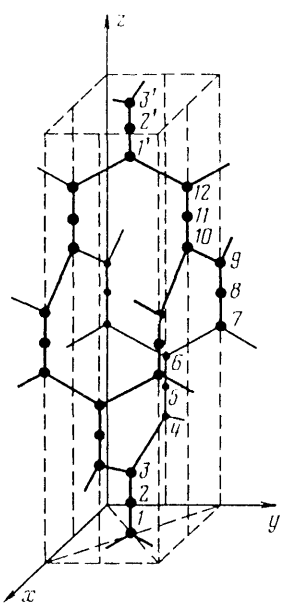
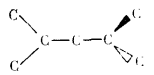


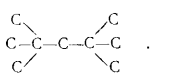
Figure 6. The crystal structure of allenocarbon; atoms *1–12* form the basis of the structure.

In the resulting structure all the valence angles are 120° and C_6 fragments of the ethylene type, with C_3 groups rotated relative to one another by 90°, are present. The C_8 net described with $r_2 = r_1$ coincides with one of the nets discussed in a monograph[104] (see also Hoffmann et al.[108]). It has a symmetry group $I4_1/amd$, a tetragonal lattice with the parameters $a = b = r_1\sqrt{3}$ and $c = r_1 + 4r_2$, contains eight atoms in the unit cell, and can be used to construct new structures. For example, we place along the sections connecting the atoms of two neighbouring layers an odd number (identical for all pairs of neighbouring atoms) n' of atoms. For $n' = 1$, the bond lengths can be chosen such that one obtains as a result a regular structure made up of fragments of the type



with two end groups rotated by 90° relative to one another. Such geometry is characteristic of compounds of the allene type[109] and we shall refer to this crystalline modification of carbon as allenocarbon (Fig. 6).

The same principle of construction has been applied by Mel'nichenko et al.[110] who used the diamond lattice for this purpose. If cubic or hexagonal diamond is represented as a structure made up of cross-linked carbon layers consisting of polycondensed carbon rings with a geometry close to that of the carbon skeleton of the cyclohexane ring, then several atoms can be placed at each cross link (the case of only one atom was considered by Mel'nichenko et al.[110]). As a result of this procedure, the layers move apart owing to the increase of the length of the interlayer cross links. However, in the case considered by Mel'nichenko et al.[110] somewhat unusual combinations of chemical bonds, made up of two tetracoordinate and one dicoordinate carbon atom, arise.



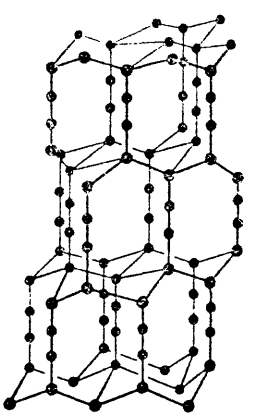
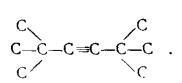


Figure 7. The crystal structure of poly-ynodiamond.[110]

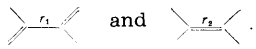
It would be more useful to distribute an odd number of atoms at the interlayer cross links, whereupon more natural structural elements of the poly-yne type would arise:



The modification obtained in this way on the basis of cubic diamond is illustrated in Fig. 7 (poly-ynodiamond).

A number of studies have been devoted to the relative stabilities of crystalline modifications of carbon. Data for the relative stabilities of planar hypothetic carbon systems of the mosaic type were presented above. It was noted that in these structures there are unusual combinations of bonds, which hinders the estimation of their lengths. On the other hand, in the $C_1(4_1)$ and $C_2(4)$ structures described in two investigations[105,106] the bond lengths can be estimated[111,112] using for this purpose the empirical relations between the internuclear distance separating chemically bound atoms and the bond type as well as data for the geometry of the carbon skeleton of hydrocarbon molecules, which are comparable to individual fragments of the crystalline modifications of carbon considered.

In structure $C_2(4)$ there are bonds of two types:



According to the data of Tatevskii and Spiridonov,[24] $r_1 = 1.48 \pm 0.02$ Å and $r_2 = 1.34 \pm 0.02$ Å. The structure $C_2(4)$ can also be described in terms of eight-membered rings (in the boat form). The geometry of these rings should be close to that of the carbon skeleton of the cyclooctatetraene molecule in which the C–C bond lengths alternate and amount to 1.462 and 1.334 Å.[113] In graphite the C–C bond length has inreased by approximately 0.02 Å compared with benzene. Similarly the C–C bond length in diamond has also increased by approximately 0.02 Å compared with cyclohexane (1.52 Å). These estimates show that in the $C_2(4)$ crystalline modification of carbon there should be bonds whose lengths are close to 1.48 and 1.35 Å.

In the $C_1(4_1)$ modification all the bonds are equivalent (in the geometrical sense). The inner bond of the C_6 fragment of the ethylene-like type, in terms of which it is possible to describe the $C_1(4_1)$ crystal structure, should be similar in its character to the C–C bond between the rings in biphenyl, i.e. its length should be close to 1.48 Å. Bearing in mind that the immediate environment of this bond persists on passing to the crystal, the C–C bond length in the $C_1(4_1)$ modification was assumed to be 1.48 Å.

Using the C–C bond lengths quoted above in the $C_1(4_1)$ and $C_2(4)$ modifications, the relative stabilities of these systems have been estimated[111,112] in relation to diamond, graphite, and two carbyne modifications: α- and β-carbyne. The relative stabilities were estimated in the following way: with the aid of three empirical relations between the bond energy and bond length or bond type:

A. From the Dewar–Schmeising formula:[114]

$$\varepsilon(r) = -\frac{1140.593}{r} + \frac{3252.755}{r^2} - \frac{1199.129}{r^3},$$

B. From the linear relation obtained on the basis of Popov and Kogan's data.[62]

C. From the dependence of the bond energy on the bond type according to Popov and Kogan's data.[62]

D. By the virial-statistical method.[115]

The bond energies in the crystalline modifications considered were calculated in the first three instances from the formula

$$E = \frac{1}{2}\sum_i n_i \varepsilon(r_i),$$

where the summation extends over all the bonds of the given atoms and n_i is the number of bonds of the given type per carbon atom.

We shall consider in greater detail the estimation of the bond energy of the crystal by the virial-statistical method, which is based on the representation of the energy of the ground state of the quantum system in the form of a functional of the electron density.[116] The electron density of the molecule (crystal) is represented approximately by the sum of the electron densities of the atoms, which were evaluated on the basis of the calculations for the atoms carried out by Clementi and co-workers.[117,118] Next it is assumed that the virial theorem holds and that the total energy can be calculated as half the potential energy.

The potential energy is calculated in terms of the approximation within the framework of the statistical theory taking into account the Coulombic, exchange, and correlation contributions.[115]

The Table presents the relative bond energies for graphite, diamond, $C_2(4)$, $C_1(4_1)$, α-carbyne, β-carbyne, and allenocarbon calculated by the four methods A, B, C, and D indicated above. It follows from the tabulated data that, for all the methods used in estimates, the $C_2(4)$ modifications should be more stable than the $C_1(4_1)$ modification and also more stable than the α- and β-forms of carbyne.

Interatomic distances and the calculated* bond energies E(C–C) for certain crystalline modifications of carbon.

Structure	r_1, Å	r_2, Å	$-E$(C–C), kcal mole^{-1}			
			A	B	C	D
Graphite	1.42	—	0.0	0.0	0.0	0.0
Diamond	1.54	—	0.3	1.0	0.9	1.5
$C_2(4)$	1.34	1.48	5.3	4.8	6.0	7.4
$C_2(4_1)$	1.48	—	14.4	14.6	23.3	32.5
β-Carbyne	1.28	—	27.0	23.1	20.9	33.6
α-Carbyne	1.38	1.20	31.8	25.6	24.0	32.8
Allenocarbon	1.31	1.51	18.4	16.4	9.1	8.0

*Methods of calculation: A) from the formula for $\varepsilon(r)$ quoted by Dewar and Schmeising;[114] B) from the formula for $\varepsilon(r)$ quoted by Popov and Kogan;[62] C) from the average bond energies;[62] D) by the method of the electron density functional.[115]

In conclusion of this Section, we shall mention a study[119] in which the relative stabilities of certain skeletal hydrocarbon oligoradicals are discussed in connection with the problem of the existence of three-dimensional carbon structures with sp^2 hybridisation of the carbon atoms.

2. The Nature of the Chemical Bonds and the Structure of the Band Spectra of Certain Hypothetical Crystalline Modifications of Carbon

It is known that diamond is a dielectric and that the width of the forbidden gap at 295 K is 5.49 eV for indirect transitions.[120] The width of the forbidden gap in the graphite spectrum is close to zero and graphite is a semi-metal. The resistivity of the graphite single crystals in the plane of the aromatic ring is smaller by several orders of magnitude than in the direction of the translational c axis. The electronic spectrum of graphite has been discussed in a number of studies[17,18,121,122] in which an extensive bibliography on graphite has also been given.

It is of interest to analyse the possible electrophysical properties of the hypothetical crystalline modifications of carbon which were discussed above. This problem has been discussed in a number of communications for modifications of the type $C_2(4)$, $C_1(4_1)$, $C_1(3_1)$, etc. We shall consider initially in greater detail the results of the study of the band spectra of the $C_1(4_1)$ and $C_2(4_1)$ structures. In estimating the band spectra of these modifications, the authors[123-125] used a model according to which the $2p$ electrons (one from each atom) located in the $2p$ orbitals (the symmetry axis of each orbital is perpendicular to the plane passing through the corresponding atoms and its three nearest neighbours) and moves in the field of the σ-skeleton of the system; the remaining three valence electrons from each atom participate in the establishment of this field. This mathematical model is analogous to that employed in the calculations for non-planar conjugated systems of the type of biphenyl in terms of the π-electron approximation. The total energy of the crystal in this model depends only on the crystal orbitals made up of the $2p$ orbitals which are not involved in the formation of the σ-skeleton. Each crystal orbital is referred to a definite wave vector **k** and is sought in the form of linear combinations of Bloch functions.

In the version of this method without adjustment for self-consistency the absolute values of the diagonal elements of the Hamiltonian were assumed to be equal to the valence ionisation potential I_p of the carbon atom. The non-diagonal elements of the Hamiltonian $H\mu\nu$ were estimated from the Wolfsberg–Helmholtz formula $H\mu\nu = -1.75\, I_p S\mu\nu$, where $S_{\mu\nu}$ is the overlap integral of $2p$ atomic orbitals of the neighbouring carbon atoms. The interaction between non-neighbouring atoms was disregarded.

For the main symmetrical directions in the first Brillouin band of the $C_1(4_1)$ modification, analytical formulae have been obtained whereby one can find the one-electron energy levels as a function of the wave vector **k**. The dispersion laws for the main symmetrical directions in the first Brillouin band corresponding to a bond length of 1.48 Å are presented in Fig. 8. The valence ionisation potential I_p was assumed to be 11.4 eV. Fig. 8 shows that the $C_1(4_1)$ modification (within the framework of the model adopted) has a band spectrum characteristic of metals. The Fermi energy is $-I_p$.

Calculation of the band spectrum of the $C_1(4_1)$ modification within the framework of the method of crystal orbitals adjusted for self-consistency in terms of the Pariser–Parr–Pople (PPP) approximation (taking into account the two-electron interaction integral γ_0 at only one centre) did not alter the conclusion that the spectrum of the $C_1(4_1)$ modification has a metallic character in the case of the restricted Hartree–Fock method; the Fermi energy increases by $\gamma_0/2$ (approximately 5 eV) when account is taken of the inter-electron interaction.

In order to estimate the influence of the non-orthogonality of the $2p$ atomic orbitals with respect to the orbitals of the σ-skeleton on the band spectrum, the one-electron energies of the $C_1(4_1)$ modification were calculated[126] in terms of the valence approximation (at the centre of the first Brillouin band). The calculation showed that the model adopted reproduces fairly correctly the qualitative features of the spectrum, because, in terms of the valence approximation, the $C_1(4_1)$ modification also has a spectrum with a metallic character.

Within the framework of the same model, the band spectrum of the $C_2(4)$ modification has been estimated.[125] The calculation was performed using bond lengths of 1.48 and 1.34 Å for bonds along and between the chains respectively. In the spectrum of the $C_2(4)$ modification there is a forbidden gap and the maximum one-electron energy in the valence band and the minimum energy in the conductivity band are attained at the centre of the first Brillouin band, i.e. when $k = 0$. It follows from the calculation that the $C_2(4)$ modification should have semiconducting properties. The width of the forbidden gap in the spectrum is 2.2 eV for the parameters selected by Nikerov et al.[124]

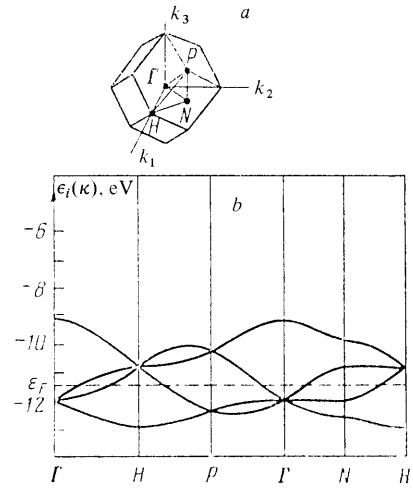


Figure 8. The band structure of the spectrum of the $C_1(4_1)$ crystalline modification of carbon: *a*) first Brillouin band (Γ—centre of band, *N*—centre of face, *H* and *P*—vertices); *b*) dependence of the one-electron energy levels $\varepsilon_i(\mathbf{k})$ on the wave vector $\mathbf{k} = (k_1, k_2, k_3)$ along the ΓH, HP, $P\Gamma$, ΓN, and NH directions; the dashed line indicates the position of the Fermi level ε_F.[123]

The spectrum of the crystalline modification constructed on the basis of the C_8 net and described above has been discussed.[108] Although in this net all the valence angles are 120°, the conjugation between the chains in different layers breaks down completely, in contrast to the $C_2(4)$ and $C_1(4_1)$ modifications considered above. The authors[108] estimated the C–C bond length for the polyene chain as 1.44 Å and obtained 2.494 Å for the distance between the polyene chains. With these values of the geometrical parameters, this modification has a density of 3 g cm^{-3}, i.e. intermediate between those of graphite and diamond. In terms of the EHM approximation, the modification has an energy spectrum of the metallic type with fairly broad bands and the energy of the Fermi level is approximately −10 eV (one should bear in mind that, in terms of the EHM approximation, this value is usually too low by 3–5 eV). Allowance for the possible alternation of the bond lengths in the polyene fragment does not introduce qualitative changes into the character of the spectrum, in contrast to the one-dimensional case.

Calculations for model macromolecular hydrocarbon systems, carried out in order to elucidate the factors influencing the band width in the three-dimensional structure, showed that the influence of the interchain interaction should be fairly strong. The authors[108] note that the Mulliken bond orders, found for the atoms located in adjacent polyene chains of the three-dimensional structure, proved to be positive, which

showed that there is an overall predominance of the bonding interaction between the chains.

3. Certain Considerations Concerning the Possibility of the Existence of New Crystalline Modifications of Carbon

In this Section of the review we shall attempt to draw certain structural analogies between the known crystalline modifications of carbon and hydrocarbons. Such analogies can be used as additional evidence in support of the possibility of the existence of new crystalline modifications of carbon.

Different hydrocarbon systems correspond to diamond and graphite, the structures of their carbon skeletons being close to the local structures of diamond and graphite. For graphite, these are benzene, naphthalene and other polyacene systems, coronene, and polycondensed aromatic hydrocarbons, while for diamond these are cyclohexane, adamantane, etc.

As mentioned above, the $C_2(4)$ structure can be described in terms of eight-membered rings characteristic of cyclo-octatetraene. The structures of cyclo-octatetraene and its octamethyl and octaphenyl derivatives have been thoroughly investigated. In all three molecules the ring has the boat conformation. The average length of a single bond in cyclo-octatetraene (1.462 Å) increases somewhat on passing to the methyl and phenyl derivatives (1.487 and 1.493 Å respectively). The length of the double bond is in the range 1.33–1.35 Å.

The synthesis of octalene—an unsaturated hydrocarbon formed by the condensation of two eight-membered rings—has been reported.[127] An interesting class of unsaturated hydrocarbons—cyclophane compounds—is known.[128] Some of these "multidecker" systems consist of two or more unsaturated six-membered rings linked by $-C_2H_2-$ bridging groups. The molecules have an interesting geometry: the planarity of the rings breaks down, the valence angles deviate from the standard values, and the system becomes strained.

If the six-membered fragments are now "replaced" by eight-membered fragments, no significant distortions of the valence angles should occur. Hypothetical systems of the type $C_{24}H_{16}$ with valence angles close to the ideal values arise. On the other hand, the carbon skeleton of the $C_{24}H_{16}$ molecule constitutes a polyhedral fragment of the $C_2(4)$ modification (Fig. 5). The synthesis of the molecule described above, which is itself of interest, might serve as additional proof of the possible existence of the $C_2(4)$ crystalline modification of carbon.

Next the crystalline modifications of carbon formed by tricoordinate carbon atoms can be described in terms of hexa-atomic fragments of the ethylene type:



In order to assess the possibility of the formation of carbon fragments of the ethylene type with rotated C_3 groups, calculations have been made[126] of the energy of the C_6 clusters of the form described above (the valence angles were assumed to be 120°) by the CNDO/2 and INDO methods as a function of the angle of rotation (the C–C bond lengths were assumed to be equal and were optimised). It was established[126] that the total energy, expressed as a function of ψ, is a minimum for $\psi = 90°$ and a maximum for $\psi = 0°$. This property of the energy is determined in the first place by the behaviour of the interaction energy of the nuclei, which is a minimum for $\psi = 90°$. On the other hand, the interelectron interaction energy is a maximum for $\psi = 90°$, but its increase is compensated by the energy of repulsion of nuclei, which decreases fairly rapidly. The equilibrium C–C bond length is close to 1.33 Å.

This calculation permits the conclusion that in the gas phase there is a possibility of the formation of C_6 clusters of the type considered; this supports the possibility of the existence in polymeric carbon of C_6 structural fragments with end groups rotated relative to one another. This possibility is also indicated by the non-planar structure of the biphenyl molecule in the gas phase: the angle of the relative rotation of the six-membered rings is approximately 42°.[129]

Thus one may conclude that diamond, graphite, and carbyne do not exhaust the possible crystalline structures which do not conflict with the ideas established at the present time concerning the ability of carbon atoms to participate in the formation of chemical bonds. Problems associated with a more detailed description of the geometry, energy relations, and spectroscopic and other physico-chemical properties of the hypothetical structures naturally remain open. All these problems can be solved, in principle, for each specific instance.

In particular, it follows from the above analysis that under normal conditions a metastable form of carbon with metallic properties can exist. It may be that some of the structures discussed above are realised among the wide variety of the existing crystalline modifications of carbon whose structure has not been established.

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