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## New Hypothetical Carbon Allotropes of Remarkable Stability Estimated by Modified Neglect of Diatomic Overlap Solid-State Self-Consistent Field Computations

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**Abstract:** A new family of yet unknown carbon modifications has been proposed. The underlying building principle consists of connecting triptycyl moieties by benzene rings in two dimensions so that 2D hexagonal nets (with regular or irregular hexagons) emerge and then connecting identical nets by simple bonds. The resulting infinite structures can be described as a mixture of  $sp^3$  and  $sp^2$  carbons and are of hexagonal nature. Some of the allotropes are crystalline, but most of these 3D solids possess only a translational symmetry in one dimension. An attempt to estimate their stability by modified neglect of diatomic overlap solid-state calculations revealed that the stability of these allotropes is comparable to that of diamond.

Carbon does exist in several allotropic forms<sup>1</sup> out of which  $C_{60}$  and  $C_{70}$  are the most recent representatives.<sup>2,3</sup>  $C_{60}$  had been predicted by Osawa<sup>4</sup> already in 1970. His paper, written in Japanese, attracted little attention due to language barriers and also due to the role of computational chemistry in those days: A quantitative and reliable confirmation of a reasonable suggestion by computational methods was intractable in 1970 (at least for molecules of that size).

Since then things have changed, and predictions or designs based on computational methods are now accepted,<sup>5</sup> especially when materials of such an enormous industrial interest as carbon modifications are considered. Various hypothetical new carbon modifications have been reported<sup>6-8</sup> out of which R. Hoffmann's metallic carbon and R. H. Baughman et al.'s "graphyne" are perhaps the best known.<sup>6</sup> Unfortunately, most of these suggested structures seem to be thermodynamically rather unstable when compared to graphite or diamond.

The recently published modified neglect of diatomic overlap (MNDO) calculations by Bakowies and Thiel<sup>9</sup> on large carbon clusters, most of them not yet known, underline the role of computational chemistry as a predictive tool to be used prior to experimentation.

In this paper we present a new set of carbon modifications consisting of infinite 3D structures derived from a common building principle. Fortunately, some representatives of this set are of crystalline nature and thus accessible to quantitative computational methods designed for the derivation of minimum energy geometries and for the estimation of the heat of formation.

### The Building Principle

The building principle of the new carbon modifications is shown in Figure 1. The two basic moieties are the triptycyl moiety (A in Figure 1) and benzene rings (B in Figure 1). In one plane the triptycyl moieties are connected by fused benzene rings so that a given triptycyl moiety is connected to each of its three neigh-

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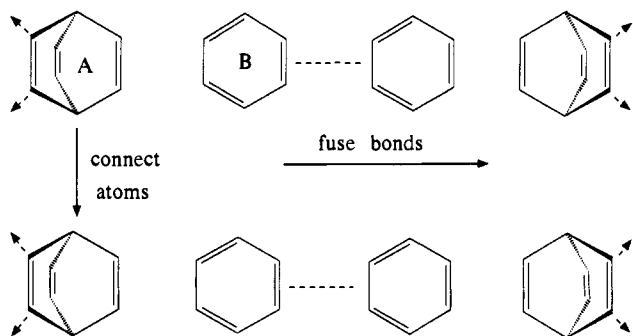
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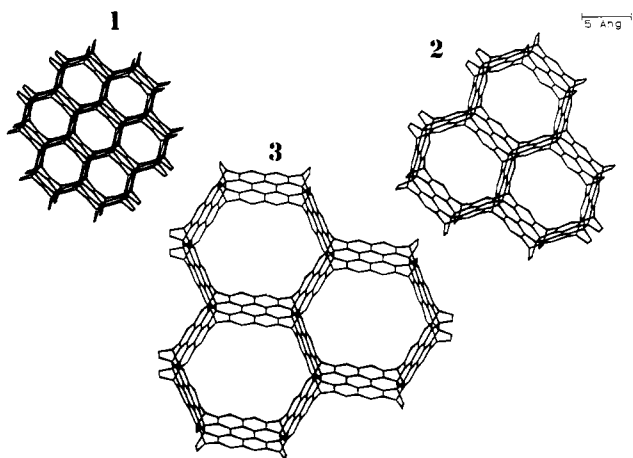
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**Figure 1.** Schematic representation of the building principle. A is a triptycyl moiety which is linked to three neighboring triptycyl moieties by fused benzene rings B. The resulting strain-free hexagonal net is perpendicular to the paper plane. Identical hexagonal nets (parallel to each other) are connected by bonds so that an infinite structure with translational symmetry in one direction will emerge. Arrows indicate growth directions.



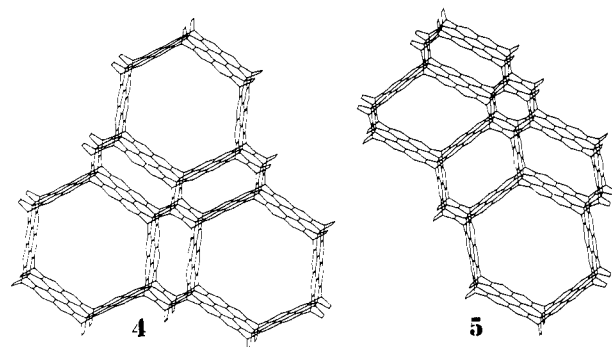
**Figure 2.** Hexagonal crystal structures on which the crystal orbital calculations have been performed. In structures 1, 2, and 3 exactly zero, one, and two fused benzene rings are located between any two neighboring triptycyl units, respectively.

boring triptycyl moieties by zero, one, or more benzene rings. The outcome could be described as a Kagome net<sup>10</sup> (a 2D hexagonal network, in our case not necessarily regular). In the third direction perpendicular to the net plane, identical nets are simply connected by chemical bonds. Since triptycyl as well as connected triptycyl units (e.g., 9,9'-bitriptycyl) are known to be rather stable,<sup>11</sup> the resulting infinite 3D structure has not acquired any significant additional strain energy.

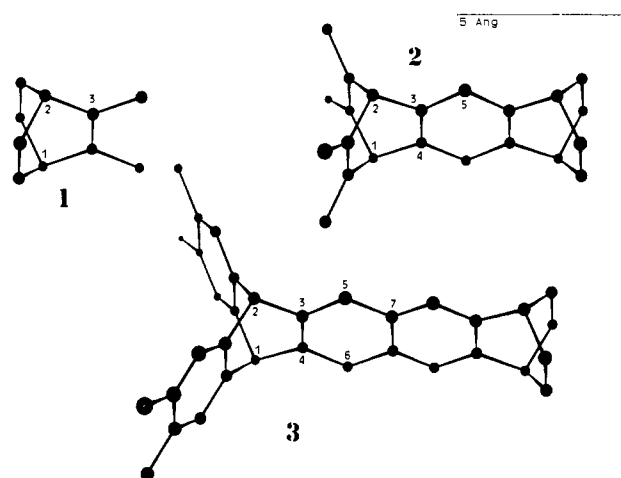
When the number of fused benzene rings between any triptycyl moiety and its three neighbors is the same, highly symmetrical crystalline structures will emerge. In Figure 2 the three lowest homologues (i.e., with zero, one, and two fused benzene rings) of these highly symmetric structure are depicted. All the calculations described below have been performed on these three structures.

When the number of fused benzene rings between the triptycyl moieties is not the same, more complicated structures like those shown in Figure 3 will result. In structure 4 (Figure 3) the high symmetry is still present although the unit cell becomes very large. The more common situation is represented by structure 5 (Figure 3) which consists of a rather chaotic assemblage of irregular hexagons in two dimensions and where translational symmetry is only preserved in the third dimension.

The common feature of all structures is the mixture between  $sp^3$  carbons occupying the corners of the hexagons and  $sp^2$  carbons occupying the edges (or faces) of the hexagons.



**Figure 3.** More complex structures of carbon modifications according to the described building principle. Structure 4 is a crystal whereas structure 5 represents the most general case where 3D translational symmetry is lost.



**Figure 4.** Unit cells corresponding to hexagonal crystal structures 1-3 (Figure 2) used in the MOSOL crystal orbital calculations. The atom numberings to which Table II refer are indicated as well.

### Computational Section

Without making use of the full symmetry of the space group to which the structures 1-3 belong, semiempirical MNDO<sup>12</sup> crystal orbital calculations are presently the upper limit of computational sophistication and the only public domain MNDO program capable of dealing with 3D crystals, in the frame of Bloch orbitals,<sup>13a</sup> is MOSOL.<sup>13b</sup>

Of prime importance is the question about the reliability of the MNDO method. Statistical analysis of semiempirical self-consistent field (SCF) calculations showed that the average unsigned error in the calculated MNDO heats of formation over a large set of carbon compounds is as high as 12 kcal/mol.<sup>14,15</sup> However, inside a generic family of compounds the error is usually much lower. For extended  $\pi$ -systems of carbons the MNDO heats of formation show errors as low as 1-2 kcal/mol per atom.<sup>9</sup> From the practical point of view the situation is not as simple, since the heats of formation of the proposed allotropes should be related to those of graphite and diamond which could hardly be considered as structural homologues of the proposed allotropes.

We have ported the VAX version of MOSOL to an IBM-RS6000/530 workstation. All the parts of MOSOL dealing with the generation of graphical output were not portable and have been rejected. For the more qualitative analysis like the graphical representation of the density of states (DOS), we made use of the EHT program package for crystals by R. Hoffmann's group.<sup>16</sup>

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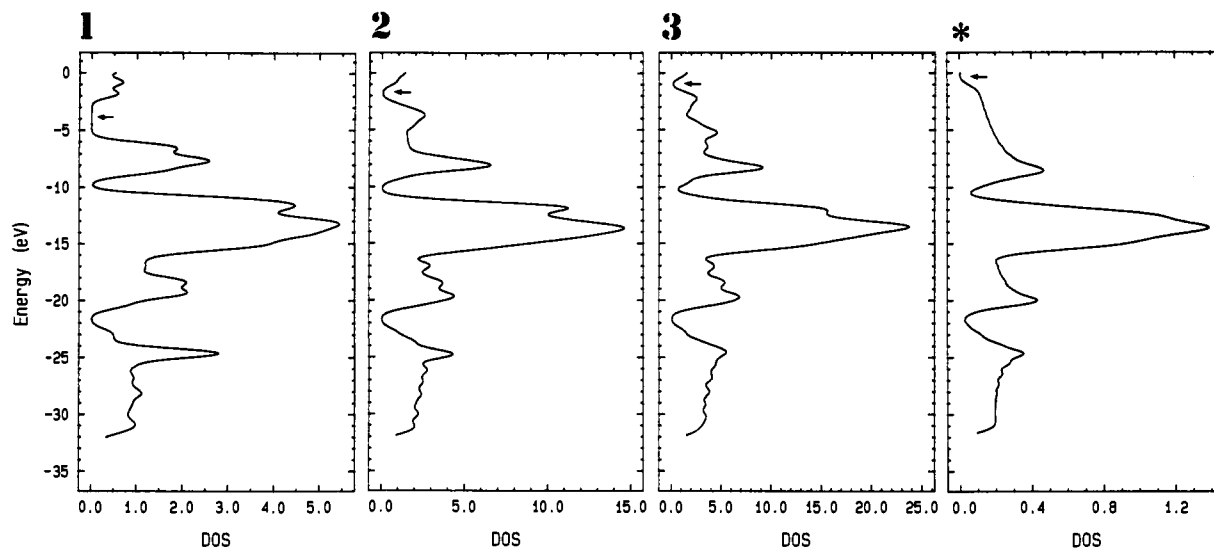


Figure 5. Density of states (DOS) of structures 1–3 and graphite (indicated by an asterisk) resulting from EHT crystal orbital calculations. The gaps are indicated by the arrows.

Table I. Parameters Used in the MOSOL Crystal Orbital Calculations

structure	no. of unit cells	<i>k</i> -points	cutoff distance for interactions
diamond	28	12 × 12 × 12	5.45
graphite (3D)	43	10 × 10 × 6	7.5
structure 1	30	6 × 6 × 7	10.0
structure 2	12	3 × 3 × 7	11.0
structure 3	13	3 × 3 × 10	13.95

The MNDO calculations were performed on structures 1–3 with the appropriate unit cells shown in Figure 4, and on diamond and graphite for control purposes. Full use of the hexagonal symmetry was made during the geometry optimization of the structures in Figure 4. For structures 1, 2, and 3 only five, seven, and nine geometrical parameters, respectively, had to be optimized by MOSOL (e.g., for structure 3 in Figure 4, the distances 1–2, 2–3, 3–5, and 5–7, the angles 1–2–3, 4–3–5, and 3–5–7, and the length of two lattice vectors). A remark to enable the reproducibility of the results below follows: The MOSOL code in subroutine SWEEP had to be modified slightly. The array dimension of FOCKK and FOCKD has been enlarged to 150 000. Further details are summarized in the next section.

The EHT calculations were done on the optimized MNDO geometries. The *k*-space was sampled by 512 (i.e., 8 × 8 × 8) equidistant grid points of equal weight (i.e., 0.1111, 0.2222, ..., 0.8888 along each direction in the reciprocal space in the appropriate units).

## Results and Discussion

Some additional parameters used in the MOSOL calculations are summarized in Table I. The resulting MNDO optimized geometries of structures 1–3 are summarized in Table II and seem to be reasonable although the short 3–5 distance of structure 3 is an indication that the optimization process has been stopped at a too early stage (for the obvious reason of cpu time: the cpu time consumed by structure 3 was extreme; about 500 h on the RS-6000/530 was needed to reduce the gradient, expressed as the scalar length (kcal mol<sup>-1</sup> Å<sup>-1</sup>), below 50). In Table III some crystal properties are reported out of which the heat of formation per atom (i.e., the relative thermodynamic stability of the material) is the most important one. It is obvious that the aromatic components will introduce an additional stability, but that structure 2 already exceeds diamond in stability was completely unexpected. It should be borne in mind that the relevant heats of formation are per atom which means for structure 3 that even when the error in the calculated heat of formation per unit cell (i.e., 34 atoms) is as large as 50 kcal/mol, it is still predicted to be more stable than diamond.

How reliable are these MNDO crystal orbital calculations? We have mentioned already in the Computational Section that the errors of the MNDO calculations are rather large when compounds from different chemical classes (i.e., belonging to different

generic families) are to be compared. This fact is reflected in the MNDO results for diamond. The calculated MNDO heat of formation of diamond<sup>17</sup> in Table III (i.e., 6.75 kcal/mol) is about 6 kcal/mol higher than the experimental value,<sup>18</sup> and the band gap for diamond of about 10 eV is not impressive either (a factor of 2 too large). Since the MNDO results for extended  $\pi$ -systems are known to be rather reliable,<sup>9</sup> we conclude that the main source of error will arise from the tetrahedral carbons contained in the proposed allotropes and that the overestimation of the heat of formation in the diamond case will appear, to some extent, in the calculated heats of formation of these proposed structures. To summarize the point, we do not think that the computational results allow for a stability ranking of the structures in Table III. We believe, however, that the computational results are sufficiently significant to conclude that structures 2 and 3 possess a stability which is comparable to that of diamond.

The computations on structures 1–3 were done under the utilization of translational symmetry, but there is no reason for a drastic change in the stability of the more probable but non-crystalline structure 5 (or any similar one).

For comparative purposes it is worth mentioning that the MNDO heat of formation of graphyne, a hypothetical carbon allotrope consisting of sp<sup>2</sup> and sp<sup>1</sup> carbons,<sup>6b</sup> is about 12 kcal/mol. The existing but rarely mentioned sp<sup>1</sup> modification of carbon, "carbyne", has a measured heat of formation as high as 8.85 kcal/mol.<sup>1c</sup>

We raise now the cardinal question: If it is true that the new carbon modifications are predicted to be as stable as diamond, why have they not yet been observed? Many physical explanations are conceivable (e.g., the lack of nucleation centers or kinetically unfavorable pathways which prohibit the growth of these structures), but the very simple reason that nobody has ever looked for such modifications should be taken into account as well. In other words, there is a good chance that these structures do exist in nature but have been overlooked.

A recent Monte Carlo quantum chemical annealing study on carbon clusters<sup>19</sup> revealed that the largest cluster, C<sub>14</sub>, always converged to a tricyclic structure with D<sub>3h</sub> symmetry which is to a certain degree similar to the triptycyl moiety present in the carbon modification studied here.

In Figure 5 the results of the qualitative EHT band calculations as DOS plots are shown for structures 1–3 and graphite. Structure 1 which contains no aromatic moiety exhibits, as expected, a

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**Table II.** Symmetry-Constrained MOSOL Optimized Geometries for the Crystals of Figure 2<sup>a</sup>

structure	Tv1	Tv3	1-2	2-3	1-2-3	3-5	4-3-5	5-7	6-5-7
1	4.809	4.236	2.698	1.534	64.55				
2	9.074	4.302	2.728	1.545	64.99	1.412	120.15		
3	13.26	4.316	2.753	1.527	64.86	1.395	120.54	1.427	60.37

<sup>a</sup>Lengths are in angstroms, angles are in degrees, and atom numbers refer to those in Figure 2. The use of the SYMMETRY option of MOSOL implies that geometrical parameters do not correspond always to bonds and bond angles. The lattice vector Tv1 is in the plane of the hexagonal net; Tv3 is perpendicular to that plane.

**Table III.** Results of the MOSOL Crystal Orbital Calculations<sup>a</sup>

structure	atoms per unit cells	HOF (total)	HOF per atom	gap (eV)	av vol per atom
diamond	2	13.5	6.75	9.823	
graphite (3D)	2	-2.02	-1.01	2.866	9.5
structure 1	10	101.0	10.1	8.016	9
structure 2	22	134.5	6.12	6.538	13.5
structure 3	34	181.8	5.35	5.006	19

<sup>a</sup>Heats of formation (HOF) are in kilocalories per mole, and the average volume per atom is in cubic angstroms.

different DOS plot than the remaining structures. The DOS of structures 2 and 3 are almost identical in the lower part of the band spectrum but deviate from each other in the upper part of the band spectrum. The DOS in the vicinity of the gaps suggest that structure 1 is an insulator whereas structures 2 and 3 tend to be semiconducting materials. More detailed projections of the DOS are possible<sup>16b</sup> but not shown in order to avoid an overinterpretation of these plots.

The range of potential industrial applications for these carbon modifications is immense since they display properties of diamond (e.g., extreme stiffness, here only in one spatial direction) and graphite (e.g., electronic properties as well as mechanical deformability in the plane orthogonal to the main axis) at the same time. The low specific gravity of the higher homologues can be deduced from the large average volume per atom given in Table III, and the large empty channels present in these homologues makes them ideal candidates for composite materials.

Apart from the large interest in C<sub>60</sub>, the main effort in the area of carbon modifications is still focused on the synthesis of diamond under high-pressure conditions. Leonidova<sup>20</sup> discovered a new hexagonal modification of carbon as a byproduct without specifying structural details. However, the reported cell parameters do not correspond to any of the modifications described above, a fact which is not surprising since we believe that our modifications are low-pressure modifications rather than high-pressure modifications.

### Summary

A new family of yet unknown carbon modifications has been proposed. The underlying building principle consists of connecting triptycyl moieties by benzene rings in two dimensions so that 2D hexagonal nets (with regular or irregular hexagons) emerge and then connecting identical nets by simple bonds. Some of the resulting infinite structures possess hexagonal crystal symmetry. The stability of these symmetrical representatives has been estimated by solid-state semiempirical SCF methods using the MNDO Hamiltonian. The calculations reveal that the new modifications are as stable as diamond. This assertion still holds true when a large error in the predicted heat of formation by the MNDO method is tolerated. There is a good chance that such carbon modifications do indeed exist in nature but have been overlooked.

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