

## Exocyclobutadieneite

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**Abstract** This communication describes a novel structural-type that could be the basis for a potentially new allotrope of C. The novel structural-type is called “exocyclobutadieneite”, and it is thus named for the 1,3-dimethylenecyclobutane generating fragment that the lattice is based upon. It is a 3-,4-connected network consisting of slightly distorted tetrahedral vertices, and slightly distorted pairs of trigonal planar vertices. The lattice can be derived from a known mineral structure called Cooperite (PtS or PdO) by a topologically isomorphic substitution of trigonal planar atom pairs, for square planar vertexes, in the parent Cooperite unit cell. As such, the new pattern bears a distinct counterpoint relationship with its sibling structural-type called the glitter lattice, which has already been described by the authors in several other papers. And whereas glitter is generated by a topologically isomorphic substitution of trigonal planar atom pairs for the square planar vertices in the Cooperite unit cell, in a fashion that extends the unit cell vertically along the crystallographic c-axis, the exocyclobutadieneite structure is generated, in counterpoint, by such an isomorphic substitution that extends the unit cell horizontally along the a- and b-axes. Both the resulting glitter and exocyclobutadieneite structural-types possess  $AB_2$  stoichiometry (where A is a tetrahedral vertex and B is a trigonal planar vertex) and both occur in the tetragonal symmetry space group  $P4_2/mmc$  (#131). The networks differ, however, in the special positions adopted by the vertices in the resultant unit cells, and in their

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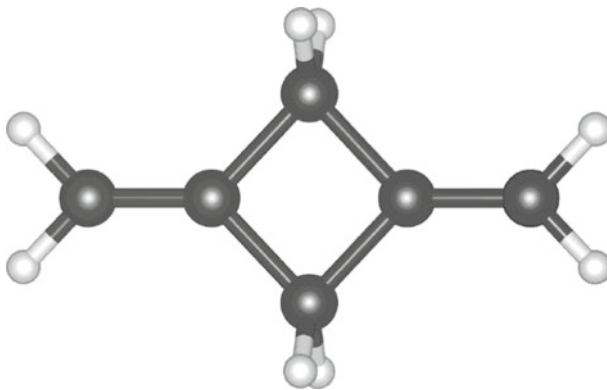
respective topology, as is evidenced by consideration of the Wells point symbols and Schläfli symbols for the 2 tetragonal networks. These differences are illustrated further in the course of the discussion to follow.

## 1 Introduction

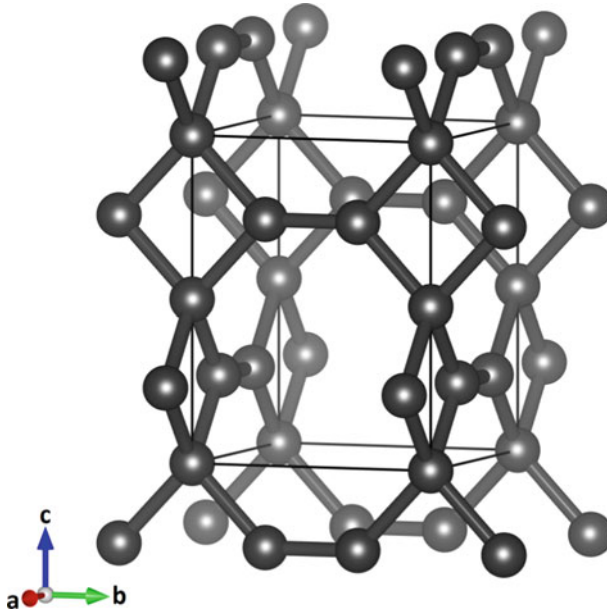
Wells described many novel crystallographic networks in his pioneering work on chemical topology [1]. Among the many 3-,4-connected networks Wells first enumerated, there was the network that is the subject of this communication, that we have chosen to call “exocyclobutadieneite” [2]. Alternatively, O’Keeffe and co-workers have enumerated many other novel structural-types as are catalogued in their Reticular Chemistry Structural Resource (RCSR) [3]. Across the innumerable network structures that are possible, exocyclobutadieneite is special because the lattice is based upon a discrete hydrocarbon generating fragment. One can thus use this hydrocarbon generating fragment, called 1,3-dimethylenecyclobutane, to elaborate the full 3-dimensional crystalline pattern. An illustration of this generating fragment molecule, created from the VASP suite of density functional theory (DFT) programs [4], is shown in Fig. 1. Figure 2 shows a VASP drawing of the corresponding exocyclobutadieneite unit of pattern [4].

The novel network whose fractional tetragonal coordinates are listed in Table 1 [4], presents a very interesting counterpoint to another 3-,4-connected network first described by Bucknum et al. in 1994 and termed the glitter network [5,6]. Glitter is alternatively based upon a 1,4-cyclohexadiene generating fragment [7,8], and a drawing of the glitter unit cell is presented in Fig. 3. Glitter has been implicated as the structure of the nanocrystalline n-Diamond and i-Carbon forms [9]. The present authors believed it would be useful to describe exocyclobutadieneite because of its close stoichiometric and structural resemblance to the glitter C network, as is described below.

Like the glitter structure-type [5,6], the exocyclobutadieneite structure-type can also be derived from the crystallographic pattern of the well-known mineral structure



**Fig. 1** Model 1,3-dimethylenecyclobutane molecule in symmetry point group  $D_{2h}$



**Fig. 2** Exocyclobutadieneite unit of pattern in symmetry space group  $P4_2/mmc$

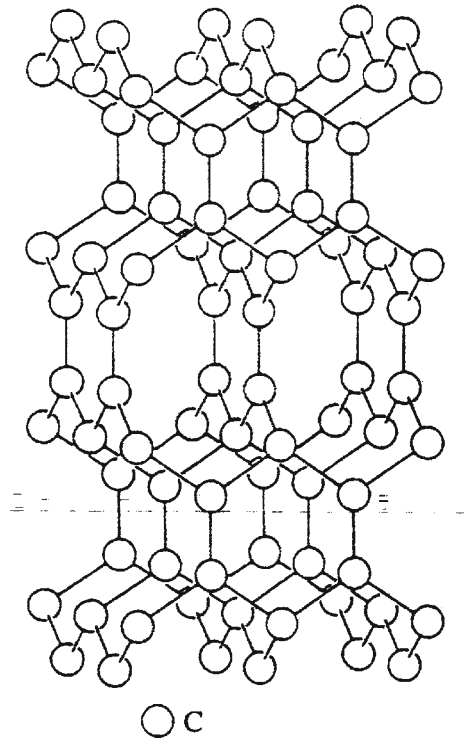
**Table 1** VASP calculated fractional tetragonal coordinates of exocyclobutadieneite pattern with a-axis 0.3439 nm and c-axis 0.4460 nm

Atom(#)	x/a	y/b	z/c
1	0	0	0
2	0.3062	0	1/4
3	0.6938	0	1/4
4	0	0	1/2
5	0	0.3062	3/4
6	0	0.6938	3/4

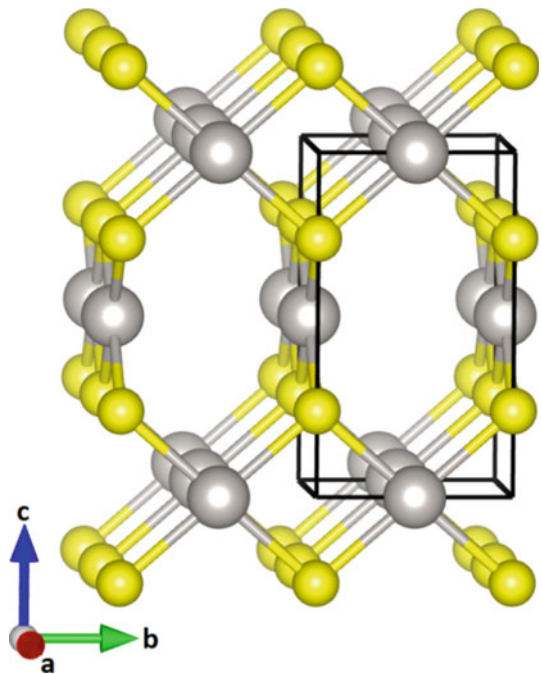
of Cooperite (PtS or PdO), as reported originally by Bannister et al. [10]. The so-called Cooperite pattern, itself, consists of an interlocking 3-dimensional (3D) array of distorted square planar and distorted tetrahedral vertices in a 1-to-1, AB-type of stoichiometry. Thus the Cooperite pattern, illustrated as a tetragonal extended structure, is shown in Fig. 4 for clarity and belongs to the  $P4_2/mmc$  (#131) tetragonal space group.

Both the exocyclobutadieneite and glitter structure-types are derived by carrying out topologically isomorphic substitutions onto the Cooperite network shown in Fig. 4, by replacing the distorted square planar vertices in Cooperite with pairs of distorted trigonal atom vertices in the resulting exocyclobutadieneite and glitter lattices. Glitter [5,6], therefore, is derived from the vertical, where vertical means along the c-axis of the tetragonal unit of pattern of the Cooperite network, insertion of parallel trigonal atom pairs of vertices, for the 2 existing, mirror-related pairs of square planar vertices present in the parent Cooperite unit cell [10]. The 2 mirror-related pairs of square planar vertices in Cooperite, in the view of Fig. 4, can alternatively be visualized within

**Fig. 3** Glitter unit of pattern in symmetry space group  $P4_2/mmc$



**Fig. 4** Cooperite unit of pattern in symmetry space group  $P4_2/mmc$



a simpler, smaller tetragonal unit cell (not shown), that is equivalent to the unit cell shown in Fig. 4. One can envision this alternative Cooperite cell from the drawing of the glitter structure-type shown in Fig. 3. Exocyclobutadieneite, as a unique counterpoint structure to glitter, is achieved, alternatively, by the isomorphic topological substitution of the same set of parallel trigonal atom pairs of vertices, for the 2 pairs of mirror-related square planar vertices evident in Fig. 4. But in this latter instance, the parallel trigonal atom pairs of vertices are directed horizontally along the a- and b-axes of the parent tetragonal Cooperite unit cell.

Because of the topologically isomorphic nature of these substitutions described above, the Cooperite, glitter and exocyclobutadieneite structure-types share the exact same space group symmetry of  $P4_2/mmc$  (#131). The stoichiometry of Cooperite is in a 1-to-1, AB stoichiometry as described above, where A is square planar and B is tetrahedral, as is evident in Fig. 4. In contrast, in the glitter and exocyclobutadieneite lattices, from the nature of the topological isomorphic substitution patterns used to generate each lattice, the resulting structural-types are in a 1-to-2,  $AB_2$  stoichiometry, where A is tetrahedral and B is trigonal planar.

## 2 Chemical topology

Exocyclobutadieneite and its structural relative glitter, and the other networks described herein can be classified and mapped according to a chemical topology scheme introduced by the crystallographer Wells [1], and later extended by us [11]. This chemical topology scheme is based upon identifying the so-called Wells point symbol for a given structural-type, where the Wells point symbol in a generic binary stoichiometry network is given by  $(A^a)_x(B^b)_y$ . In this notation, the bases represent the circuitry within the structure as being in “A-gon” and “B-gon” polygonal circuits, the superscripts represent the respective connectivities of the vertices in the structure as “a-connected” and “b-connected”, and finally the subscripts identify the stoichiometry of the structure in terms of “x” structural components of topology “A<sup>a</sup>”, in a ratio with “y” structural components of topology “B<sup>b</sup>”, within the respective unit of pattern. From analysis of this notation one can determine a weighted average polygon size in the structure, identified as “n” in Eq. (1) below, and a weighted average connectivity in the structure, identified as “p” in Eq. (2) below.

$$n = (a \cdot A \cdot x + b \cdot B \cdot y) / (a \cdot x + b \cdot y) \quad (1)$$

$$p = (a \cdot x + b \cdot y) / (x + y) \quad (2)$$

These parameters called the polygonality “n” and the connectivity “p” are characteristic of each and every one of the polyhedra, tessellations and networks, and once identified they can be used to heuristically map the various structures in a construction briefly described here. Thus the polyhedra are characterized by a simple mathematical formula due to Euler [11], shown as Eq. (3) below, that forms the basis for this heuristic mapping construction. In Eq. (3) the number of vertices in the polyhedron is identified as “V”, and the number of edges is identified as “E”, and the number of faces in the polyhedron is identified as “F”.

**Table 2** Chemical topology mapping of structures

n	p						
	3	4	5	6	7	8	...
3	t	o	i	(3,6)	(3,7)	(3,8)	
4	c	(4,4)	(4,5)	(4,6)	(4,7)	(4,8)	
5	d	(5,4)	(5,5)	(5,6)	(5,7)	(5,8)	
6	(6,3)	(6,4)	(6,5)	(6,6)	(6,7)	(6,8)	
7	(7,3)	(7,4)	(7,5)	(7,6)	(7,7)	(7,8)	
8	(8,3)	(8,4)	(8,5)	(8,6)	(8,7)	(8,8)	
⋮							

$$V - E + F = 2 \quad (3)$$

And so for the various polyhedra, one can thus transform Eq. (3) into Eq. (4) shown below, by employing the alternative, though rigorous and equivalent, set of definitions of “n” and “p” for the polyhedra; given as the polygonality  $n = 2E/F$ , and the connectivity  $p = 2E/V$ .

$$\frac{1}{n} - \frac{1}{2} + \frac{1}{p} = \frac{1}{E} \quad (4)$$

It is thus Eq. (4), together with the definitions of the weighted average polygonality “n”, and the weighted average connectivity “p” in Eqs. (1) and (2) that can be used heuristically to create a topology mapping of all structures, as shown below in Table 2. For reference, note in Table 2 that “t” is the tetrahedron, and “o” is the octahedron, and “i” is the icosahedron, and “c” is the cube, and “d” is the dodecahedron. Note also, for reference, in this topology map that the entry (6, 3) corresponds to the graphene sheet, and the entry (6, 4) corresponds to the diamond polytypes. The Platonic polyhedra thus anchor this heuristic construction and provide the basis for the structural organization of matter. For details of this construction the reader is referred to our earlier work. [11]

For the exocyclobutadieneite structure-type, discussed in this communication, the  $AB_2$  stoichiometry translates into a Wells point symbol of  $(4^2 10^4)(4 \cdot 10^2)_2$  and thus a Schläfli symbol of  $(8, 3^{1/3})$ , see Fig. 2. The Schläfli symbol for exocyclobutadieneite at  $(8, 3^{1/3})$  is curiously related to that of glitter, as is given by  $(7, 3^{1/3})$ . The Wells point symbol for the glitter network is  $(6^2 8^4)(6^2 8)_2$  and we therefore have distorted 3- and 4-connected, trigonal planar and tetrahedral vertices, exclusively in 6-gon and 8-gon circuits in glitter, versus 3- and 4-connected distorted trigonal planar and tetrahedral vertices, exclusively in 4-gon and 10-gon circuits in exocyclobutadieneite. The topological form index,  $l = n/p$  [12], indicates that exocyclobutadieneite at 2.4, is more open as a network pattern than is glitter at 2.1, but only slightly so, where the glitter network corresponds on average to 7-gons, and the exocyclobutadieneite structure corresponds on average to 8-gons. From the Schläfli symbols (n, p) derived from such

Wellsean structures as that shown as glitter and exocyclobutadieneite here, it is clear that they would lie *diagonally* from those entries for the regular structures in Table 2, as their Schläfli symbol  $(n, p)$  is comprised of fractional connectivity  $p$  and nominally fractional polygonality  $n$ . Thus the exocyclobutadieneite structure is found to be a more topologically open lattice by analysis of its Schläfli symbol  $(n, p)$  and corresponding topological form index,  $n/p$ , than is glitter. And this leads to some intuitive differences in its physical properties including its density.

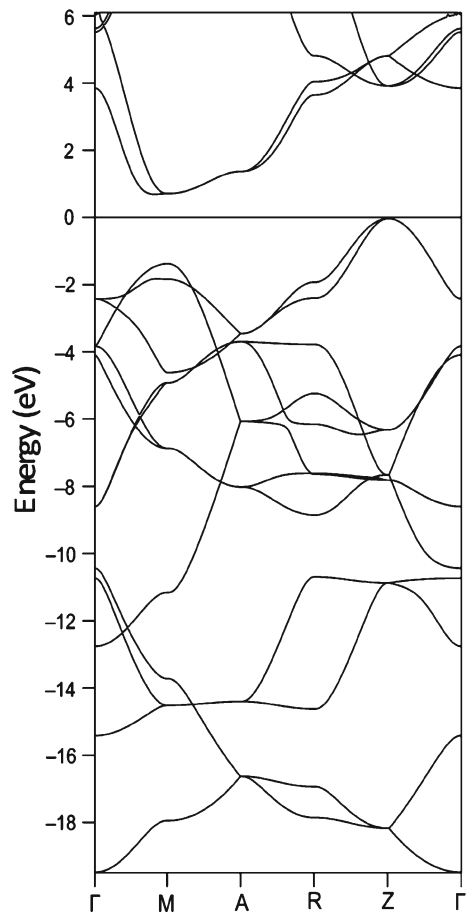
### 3 Density functional theory results for exocyclobutadieneite

Density Functional Theory (DFT) using the Vienna *ab initio* Simulation Package (VASP) [4] was used to optimize the geometry of the exocyclobutadieneite network and to calculate its band structure, density of states (DOS) and determine its relative stability with respect to graphite, diamond and glitter. Thus the crystal structure optimizations and band structure calculations were performed using VASP [4], employing the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional of the generalized gradient approximation (GGA) [13]. The core-valence electron interaction was treated by the projector-augmented wave method (PAW) [14, 15]. The PAW potentials contain carbon  $2s^2, 2p^2$  valence electrons. The cut-off energy for the plane waves was set to 1,000 eV and the Brillouin-zone integration was sampled using a  $15 \times 15 \times 15$  k-point mesh generated by Monkhorst-Pack scheme. All atomic positions and lattice vectors were fully relaxed until the forces converged to  $10^{-3}$  eV/Å.

Exocyclobutadieneite in the geometry optimized by VASP is tetragonal and lies in the space group  $P4_2/mmc$  (#131), with the a-axis at 0.3439 nm and the c-axis at 0.4460 nm [4]. The volume of the unit cell is thus  $5.275 \text{ nm}^3$ . The optimized lattice has a DFT density of  $2.268 \text{ g/cm}^3$  which is almost identical to that of graphite at  $2.27 \text{ g/cm}^3$  [16]. The 3-, 3-connected C–C bond lengths are 0.1332 nm, and the 3-,4-connected C–C bond lengths are 0.1534 nm, with the tetrahedral angles being 121.9 degrees and the trigonal planar angles being 133.4 degrees. The DFT coordinates of the 6 atoms in the exocyclobutadieneite unit cell are given in Table 1 in a unit cell setting chosen to be consistent with the earlier work on the glitter network [5,6]. The Wyckoff positions of the C atoms in an alternative unit cell setting of the optimized network are: (0.00, 0.00, 0.25) in 2e and (0.3062, 0.00, 0.50) in 4l.

The VASP electronic band structure is shown in Fig. 5 below, and the accompanying density of states (DOS) is shown in Fig. 6 [4]. The band structure consists of 24 bands, with 10 bonding  $\sigma$  bands and 2 bonding  $\pi$  bands and 10 antibonding  $\sigma^*$  bands and 2 antibonding  $\pi^*$  bands. This distribution of bands arises from the symmetry adapted mixing of the s,  $p_x$ ,  $p_y$  and  $p_z$  atomic orbitals on the 6 C atoms in the unit cell of exocyclobutadieneite. For comparison one can consider the band structure of the sibling glitter pattern, as glitter is also comprised of 6 C atoms in its unit cell it contains an analogous distribution of 12 bonding and 12 antibonding bands in its electronic structure. In both exocyclobutadieneite and glitter the 12 bonding bands are occupied, while in glitter a 13th  $\pi^*$  band is partially occupied [5,6]. Therefore however, where exocyclobutadieneite and glitter differ is in their band profiles at their respective Fermi levels, with exocyclobutadieneite being calculated as a small indirect

**Fig. 5** VASP calculated electronic band structure of exocyclobutadieneite

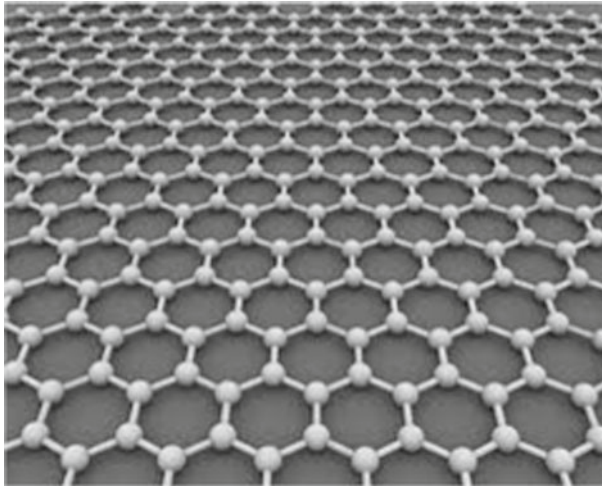
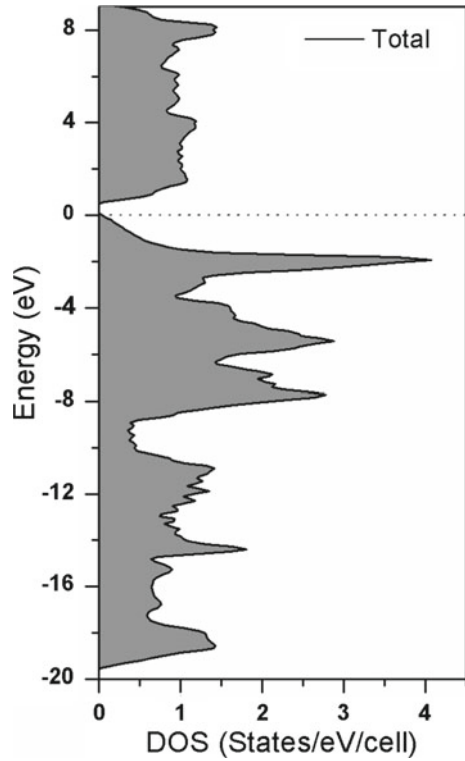


band gap insulator with a band gap of about 0.5 eV, while glitter is calculated to be a metallic C allotrope. Thus where exocyclobutadieneite would be transparent, the sibling glitter pattern would be opaque in appearance with a density of states at its Fermi level.

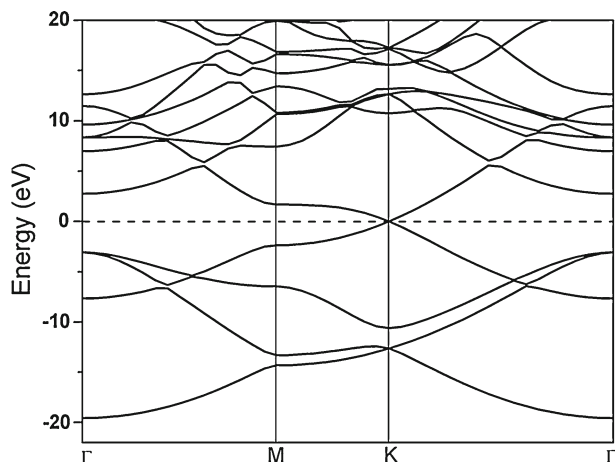
It is also interesting to consider the band profiles of exocyclobutadieneite and graphite since the 2 allotropes of C present themselves as being alternative allotropes of C with almost identical densities. An idealized drawing of the graphene sheet is shown in Fig. 7. Evidently the packing of C atoms within the graphite and exocyclobutadieneite unit cells is virtually homologous, giving rise to a density of about  $2.27 \text{ g/cm}^3$  in each respective pattern, as described above. However graphite has a semi-metallic band profile, where there is  $1 \pi$  and  $1 \pi^*$  band that just touch each other at one symmetry point (K) in the Brillouin zone, see Fig. 8. Thus as a semi-metal graphite/graphene is opaque and dark gray-black in appearance. As Figs. 5 and 6 reveal, though, in contrast the exocyclobutadieneite network is a small indirect band gap insulator and will be transparent. An interesting twist in this analysis is that



**Fig. 6** VASP calculated density of states (DOS) of exocyclobutadieneite



**Fig. 7** Graphene tessellation in plane group  $p6mm$



**Fig. 8** Band structure of graphene

graphene is well-known to be conjugated in 2D and this confers on it stability, while in contrast here the exocyclobutadieneite lattice can be seen to be spiroconjugated in essentially 3D, like the glitter pattern described above [17]. It is clear from the stability discussion to follow, that exocyclobutadieneite does not achieve stability from spiroconjugation to compare with the stability that graphite achieves through conjugation. But it is clear that the spiroconjugation in glitter confers a superior stability to exocyclobutadieneite, and this is presumably because of the  $p_{\sigma}$  and  $p_{\text{spiro}}$  constructive interactions present in glitter, where exocyclobutadieneite only has  $p_{\text{spiro}}$  interaction and minimal  $p_{\sigma}$  interaction. One can compare the unit cells of these allotropes of C to see this difference.

Finally we address the relative stabilities of these C allotropes described above. Herein we provide a listing of the VASP calculated stabilities of graphite, diamond, glitter and exocyclobutadieneite [4]. Graphite is at the zero on the energy scale with a VASP calculated stability of  $-9.230$  eV/C atom, diamond is the next most stable C allotrope in this series with a stability of  $-9.098$  eV/C atom, then comes glitter with a stability of  $-8.640$  eV/C atom, and finally exocyclobutadieneite with a computed stability of  $-8.537$  eV/C atom. Thus with graphite at the origin, diamond lies just  $0.1320$  eV/C atom above graphite, while glitter is calculated to be  $0.5890$  eV/C atom above graphite, and where finally exocyclobutadieneite is  $0.6930$  eV/C atom above graphite. A lesson from the fullerenes, which lie approximately  $0.3$  eV/C atom above graphite, is that stability is not strictly thermodynamic and that kinetically persistent structures of C are possible, that are nonetheless not thermodynamically favored. Still it is clear that graphite and diamond are thermodynamic sinks and that it would be difficult to achieve the glitter and exocyclobutadieneite patterns in any thermodynamic synthesis, such as conventional static high pressure-high temperature methods. A prediction of a kinetically driven synthesis of glitter has been reported by the authors earlier, however [18]. It is believed that the suggestion of the exocyclobutadieneite pattern in the present report is a useful exercise because of its unique counterpoint chemical

topology to glitter, and the fact that it is built upon a hydrocarbon generating motif (1,3-dimethylenecyclobutane), and because it has interesting electronic and mechanical properties including possibly being transparent and, with its relatively short bond lengths and high coordination number, it could be superhard [19].

In this connection, with respect to the claim of superhardness, Cohen et al. have proposed a semi-empirical expression for estimating the zero- pressure bulk modulus,  $B_0$ , in crystalline ionic-covalent networks [19]. The formula due to Cohen et al. is shown below as Eq. (5):

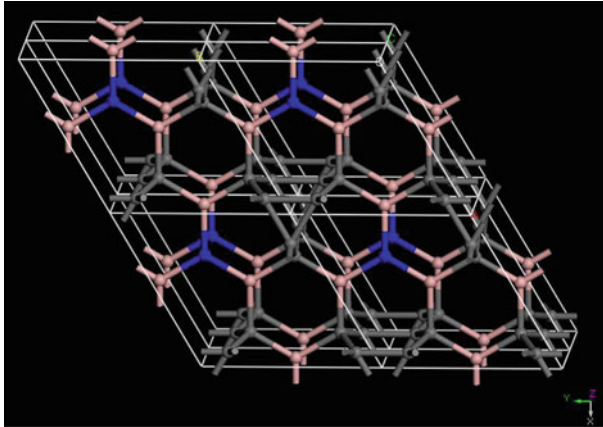
$$B_0 = \left( \frac{1972 - 220(I)}{(d)^{3.5}} \right) \left( \frac{(N_c)}{4} \right) \quad (5)$$

In Eq. (5) the empirical parameters are (1) the ionicity,  $I$ , which is just “0” for exocyclobutadieneite as a C allotrope, (2) the coordination number,  $N_c$ , which is just  $3^{1/3}$  for exocyclobutadieneite, as described above, and (3) the averaged bond distance,  $d$ , which is a weighted average of the single bond lengths (0.1534 nm) and the double bond lengths (0.1332 nm) in the exocyclobutadieneite unit cell, with the averaged value being about 0.1466 nm. By inserting these parameters into Eq. (5) a value of about 430 GPa for  $B_0$  is obtained for the exocyclobutadieneite pattern as a C allotrope. This result is remarkable, and together with its potential transparency, places exocyclobutadieneite as among the strongest possible crystalline lattices.

## 4 Conclusions

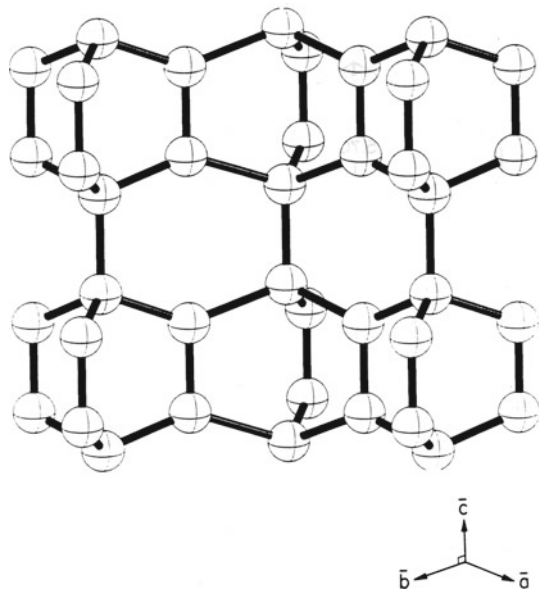
Exocyclobutadieneite is thus the first member of a related series of crystalline patterns built upon homologous hydrocarbon generating fragment molecules. Such patterns are of great interest as potential C allotropes, as the graphene sheet is based upon a benzene-like motif, and the diamond polytypes are generated based upon a cyclohexane-like motif. Thus as has been described earlier in Sect. 1, exocyclobutadieneite is built upon a 1,3-dimethylenecyclobutane motif. The next member of this series is called trigohexagonite [20] and it is built partially on a 1,3,5-trimethylenecyclohexane motif as shown in Fig. 9. The glitter pattern, shown in Fig. 3, is the next member of this series [5,6] and it is built upon a 1,3,5,7-tetramethylenecyclooctane generating fragment (or alternatively built from a 1,4-cyclohexadiene generating fragment). And finally a fourth member of this series of crystalline patterns is the so-called hexagonite pattern [21], shown in Fig. 10, which can be generated based upon a 1,3,5,7,9,11-hexamethylenecyclododecane generating fragment (or alternatively the network can be generated from a barrelene motif). Crystallographic evidence has been presented by the authors suggesting the high-pressure synthesis of this novel C allotrope has been achieved with nanotube starting material [22]. And there may, in fact, be higher members of this series of homologous crystalline patterns, and the tantalizing possibility of enumerating further network structures in this series will be the subject of future investigations.

Exocyclobutadieneite presented in this paper is thus an interesting proposal for a possible C allotrope. The network has a DFT optimized density essentially identical to



**Fig. 9** View of trigohexagonite crystalline pattern perpendicular to the **ab**-plane of the lattice, lying in symmetry space group  $P-6m2$

**Fig. 10** Lateral view of hexagonite crystalline pattern, view is parallel the **ab**-plane, lying in symmetry space group  $P6/mmm$



graphite, and where graphite is conjugated in 2D its electronic structure, exocyclobutadieneite is spiroconjugated in 3D in its respective electronic structure. Exocyclobutadieneite is a small indirect band gap insulator and as such it should be transparent in appearance, analogous to the wide direct band gap insulator diamond. Finally exocyclobutadieneite presents an interesting counterpoint in its chemical topology to the previously described glitter pattern [5,6], as has been described in Sect. 2. A stability analysis described in Sect. 3 suggests that exocyclobutadieneite may not readily be created in a thermodynamic synthesis, but the existence and ubiquity of the fullerenes

implies that there may possibly be a kinetic route to creating these novel C forms like exocyclobutadieneite.

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