Squaroglitter: A 3,4-Connected Carbon Net

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S *Supporting Information*

ABSTRACT: Theoretical calculations are presented on a new hypothetical 3,4-connected carbon net (called *squaroglitter*) incorporating 1,4 cyclohexadiene units. The structure has tetragonal space group *P4/mmm* (No. 123) symmetry. The optimized geometry shows normal distances, except for some elongated bonds in the cyclobutane ring substructures in the network. Squaroglitter has an indirect bandgap of about 1.0 eV. The hypothetical lattice, whose density is close to graphite, is more stable than other 3,4-connected carbon nets. A relationship to a (4,4)nanotube is explored, as is a potential threading of the lattice with metal needles.
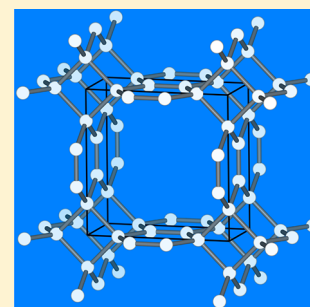
1. INTRODUCTION

Diamond and graphite, existing in a variety of polytypes, are, along with the menagerie of fullerenes, the well-known stable (or metastable, but kinetically most persistent, as in the case of buckminsterfullerenes) allotropes of carbon. A variety of other carbons have been studied experimentally, the most interesting of these perhaps being the polyacetylenoid (or cumulenoid) *karbin*;[1] but few of these alternative carbons can be made reproducibly. The number of hypothetical carbon allotropes is very large, testifying to (among other things) how much easier calculations are than experiment. We add here another network, a 3,4-connected one we will call *squaroglitter*.

There is a multitude of 4-connected networks. For instance, every zeolite or quartz network (and there are many) can be transformed to a 4-connected network by deleting the oxygens. Barring very strained topologies, these will all be insulators or semiconductors, and they will be substantially less stable than diamond, even as they might approach it in density — the cyclohexane-type rings in the diamond polytypes are pretty free of strain. Space-filling all-3-connected networks are more interesting electronically, as some are potentially metallic.[2] They can be denser than graphite (therefore the potential of synthetic access to them at high pressure), but in the cases at hand that density is associated with unfavorable, destabilizing $\pi-\pi$ overlap.

3,4-Connected networks are an interesting compromise, in which some of the carbons are graphitic (coming usually in at least coplanar pairs), and others are 4-connected, diamond-like. Their density is usually intermediate between that of graphite and of diamond, and the combination of 3- and 4-connection often leads to unstrained arrangements. We have suggested earlier a variety of these, in which through-space interactions between CC double bonds are just below that found in graphite, with resulting semiconducting or metallic behavior,[3,4] and still

other networks have been suggested by other researchers.[5,6] The network described in this communication is related to two other 3,4-connected systems based on a 1,4-cyclohexadieneoid hydrocarbon generating fragment, named colloquially as *glitter*[4] and *isoglitter*.[7]

2. THE SQUAROGLITTER STRUCTURE

Squaroglitter is generated from the template of the 3-connected tessellation known as the square-octagon tiling (Figure 1; Wells
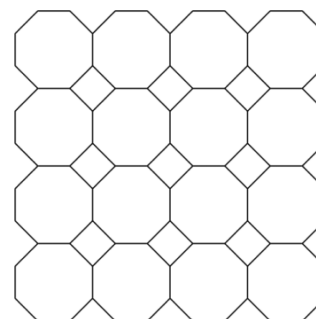

Figure 1. The 4.8² tessellation.

point symbol 4.8²).[8] To get a 3-dimensional net, one repeats the tiling along the *c* axis and then inserts the 1,4-cyclohexadieneoid hexagonal rings between the planar nets, along the edges shared by octagons in the pattern, with positions 3 and 6 in the 1,4-cyclohexadiene ring located at the termini of these respective edges. The squares are left as CC bonds; each square vertex

becomes 4-coordinated in this construction. The *squaroglitter* lattice[9] has the Wells point symbol of $(6^3)(4.6^5)$.

It is evident that this construction principle can be extended; other 3-connected plane nets like 6^3 and 4.6.8 would appear to be possible templates for generating glitter patterns based upon a 1,4-cyclohexadiene building block. The electronic structure of such nets has not yet been studied; they are likely to be less dense than graphite. We note that the *squaroglitter* structure as well as some other networks related to it have been recently described, in work independent of ours, by Zhao et al. and Hu et al.[6]

The three-dimensional structure of *squaroglitter* is shown in Figure 2. It contains planar 1,4-cyclohexadiene rings condensed
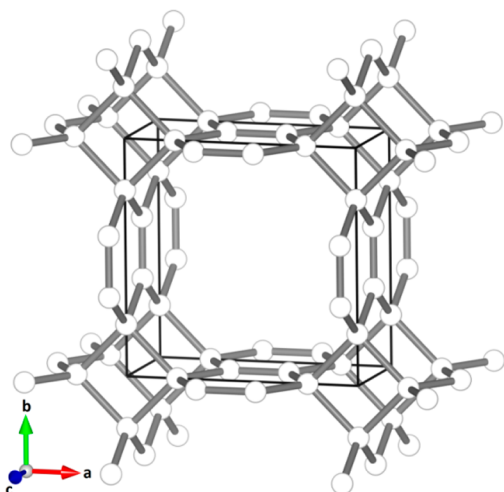

Figure 2. Optimized crystal structure of *squaroglitter*.

along the edges of their 3-connected carbon atoms forming polyacene-like (but unconjugated) one-dimensional arrays. These arrays span the four adjacent faces of the tetragonal unit cell and are three-dimensionally interconnected by 4-connected sp^3 carbons. The 4-connected carbons form cyclobutane rings. The tubular channels along the *c*-axis are apparent. As previously mentioned the space group of this tetragonal structure is *P4/mmm*.

Optimization of the geometrical parameters of the structure (the methodology, DFT with the VASP software, is detailed in the Appendix at the end of this paper) leads to the crystallographic data given in Table 1. The gravimetric density of the optimized *squaroglitter* (2.32 g/cm^3) is just a little higher than graphite (2.26 g/cm^3) but much lower than diamond (3.52 g/cm^3). So the prospects of synthesis of such a structure under pressure are not great; there are denser 3-,4-connected nets, for example *glitter*[4] and *isoglitter*.[7] The cyclohexadienes are separated (across the channel) by 5.24 Å (equal to the length of $a = b$ lattice

Table 1. DFT-PBE Optimized Crystallographic Data for *Squaroglitter*

	space group	*P4/mmm* [# 123]	
	a (Å)	5.237	
	c (Å)	2.509	
	V (Å^3)	68.81	
	ρ (gm/cm^3)	2.32	
atom (site)	x	y	z
C1 (4m)	0.62871	0.0	0.5
C2 (4l)	0.21773	0.0	0.0

parameter), much longer than the interlayer distance in graphite (3.35 Å).

The optimized CC distances are as follows: C(3)C(3) = 1.348 Å, C(3)C(4) = 1.490 Å, and C(4)C(4) = 1.612 Å. The notation C(3) and (C4) refers to three and four connected sp^2 and sp^3 carbon sites, respectively. The C(4)C(4) distance is elongated relative to diamond (1.544 Å); otherwise there is little evidence of strain in the structure, given the cyclobutane rings. A comparison to the geometries of cyclohexadiene and cyclobutane building blocks is given in the Supporting Information (SI) to this paper.

Squaroglitter is calculated to be at the DFT-PBE level of theory 5.0 kcal/mol thermodynamically less stable than diamond. The PBE functional generally predicts reasonable geometries and binding energies.[10] For graphite the calculated density is low, as the interlayer spacing, due to dispersion forces, is too large. Using the PBE-D2 functional, designed to correct empirically for dispersion energies, may be seen to improve the calculated density of graphite but makes little difference to the relative energies and densities of the other phases. The relative energy comparisons with selected other 3,4-connected carbon nets relative to graphite are tabulated in Table 2. *Squaroglitter* is the most stable of the 3,4-connected carbons listed in Table 2.

The reasons for the overall relative stability of 3,4-connected nets are given in the Introduction. In contrast to *glitter*, *squaroglitter* has no repulsive interaction between nonbonded π systems. The calculated bulk modulus of *squaroglitter* is 260 GPa, much higher than graphite (30 GPa) but smaller by a factor of 2 than diamond (443 GPa).

The calculated phonon dispersion spectrum of *squaroglitter* has no imaginary phonon modes (see Figure 3), implying that the *squaroglitter* structure is dynamically stable. The phonons at 1700−1600 cm^{-1} are due to C(3)C(3) stretching modes (see contributions to phonon density of states, DOS, in Figure 3). These modes are stronger than C(3)C(3) stretching modes in graphite (this study: 1533 cm^{-1}, experiment:[15] 1575 cm^{-1}), a difference that can be attributed to the shorter, more localized C(3)C(3) distances in *squaroglitter*. If *squaroglitter* were to be synthesized, it could be detected by these characteristic modes (among others).

The literature contains experimental and theoretical studies of a variety of compressed graphites, with indications that the materials contain both 3-coordinate and 4-coordinate carbons.[16] However, the computed diffraction pattern of *squaroglitter* does not match these (see Figure S3).

3. ELECTRONIC STRUCTURE

Squaroglitter is computed to be an insulator with an indirect (at M and Z special points) DFT-PBE band gap of 1.0 eV, as shown in Figure 4. As DFT underestimates the band gaps by about 40−50%,[17] the reported gaps here should be taken as a lower bound. The bands are quite dispersed and spread throughout the valence band (E_f to −22 eV). The 3-connected carbon 2p states are dominant directly below and above the Fermi level, consistent with these states being derived from π and π^* levels of the cyclohexadienes.[3,4] The SI gives a more detailed analysis of the states directly below and above the Fermi level; further details may be found in the Ph.D. dissertation of N. M. Gerovac.[18]

4. A RELATED (4,4)NANOTUBE

If one cuts out of the *squaroglitter* structure a single channel bounded by carbon atoms, one actually generates a (4,4)-
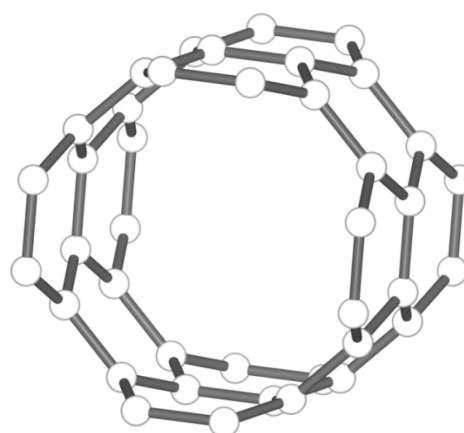
Table 2. Relative Energy Per Atom (RE) in kcal/mol and Gravimetric Densities (Density) in gm/cm³ of Selected Carbon Allotropes at 1 atm at PBE and PBE-D2 Level of Theory[b]

structure	no. of atoms/cell	RE[PBE]	RE[PBE-D2]	density[PBE]	density[PBE-D2]
graphite	4	[0]	[0]	1.76[a]	2.36
(experiment)[11]				(2.26)	(2.26)
diamond	8	3.0	0.7	3.50	3.52
(experiment)[12]		(0.5)[13]	(0.5)	(3.52)	(3.52)
squaroglitter	8	8.0	7.6	2.32	2.33
glitter[4a]	6	13.6	11.8	2.96	2.98
exocyclobutadieneite[14]	6	16.0	15.4	2.27	2.30
hexagonite[4b]	10	13.1	12.8	2.36	2.37
isoglitter[7]	8	10.0	8.1	3.01	3.05

[a]The theoretical density for graphite is too low, as a result of this level of theory not taking proper account of dispersion forces. [b]Available experimental results are listed in parentheses.
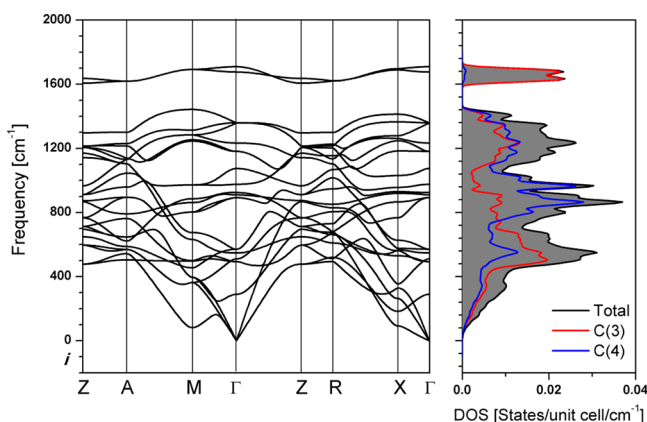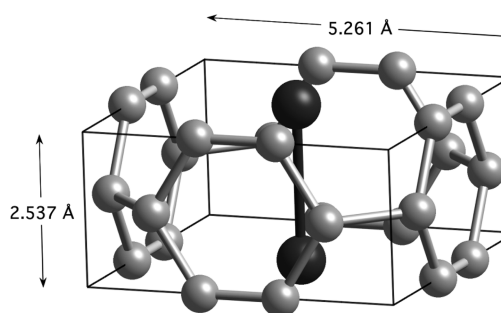

Figure 3. Calculated phonon dispersion spectrum and phonon DOS of *squaroglitter*.
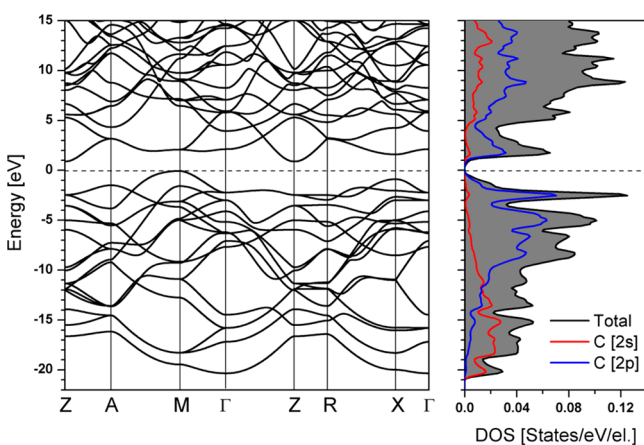
Figure 4. Calculated electronic band structure and DOS of *squaroglitter* at 1 atm. The dotted line corresponds to the Fermi energy level (E_F).

Figure 5. Optimized geometry of (4,4) nanotube shown in a $1 \times 1 \times 2$ cell.

5. FILLING THE SQUAROGLITTER STRUCTURE WITH METAL NEEDLES

The channels of the structure pose a challenge; can they be threaded? Transition metals were placed in the channels, as illustrated by the PdC_4 cell shown in Figure 6. The addition of the metal needle had very little effect upon the size of the unit cell,

Figure 6. PdC_4, a palladium filled squaroglitter variant.

nanotube. The surgery without healing leads to a structure 14 kcal/mol above graphite; optimization results in a structure 6.2 kcal/mol unstable. We show a slice of the nanotube in Figure 5. The six-membered rings are all equivalent and nonplanar in the nanotube then, with CC 1.43 Å. This nanotube is calculated to be metallic, in accordance with expectations for an armchair (n = m)nanotube.[19] Condensation of such nanotubes to *squaroglitter* has been recently described by Zhao et al. and Hu et al.[6]

expanding in the *a,b* plane by only 0.4% and by 1% in the *c* direction.

The structures that emerged were indeed metallic, but close examination of the DOS (see SI, Figure S6) showed very little mixing between Pd 4d orbitals and the carbons. The problem is that the channels are too big -- distance between the palladiums

and the centers of the C—C bonds around them is 2.63 Å, which is substantially longer than a typical organometallic separation. This is the reason for such little interaction between the needle and the framework. This was true for other transition metals as well. We are continuing to think about other ways to fill the channels with interacting metal chains and constructing other variants of squaroglitters (see SI, Figure S7).

Calculations were performed for most transition metals. In every case, a similar band structure was encountered. We observed an increase in the bandwidth of the d bands when moving along a row from right to left as well as down a column. Yet in spite of this, interactions between the metal and the carbon lattice were nonexistent.

6. SUMMARY

We calculate the geometry and electronic structure of a new 3,4-connected tetragonal carbon net — *squaroglitter*, adding another, relatively stable hypothetical carbon allotrope to the collection of such proposed models. The net emerges as a low band gap insulator.

■ APPENDIX. THEORETICAL METHODOLOGY

Electronic structure calculations are done using density functional theory (DFT) as implemented in the Vienna *ab initio* Simulation Package (VASP).[20] Perdew-Burke-Enzerof (PBE) functional[21] as the exchange-correlation energy functional and Projector Augmented Wave (PAW) method[22,23] for electron-ion interaction were used in our calculations. The calculations were also done with a PBE-D2 functional that includes an empirical correction for dispersion energies.[24] A plane-wave basis set cutoff of 1000 eV, self-consistent field tolerance of 0.1×10^{-6} eV/atom are used, and the Brillouin zone is sampled on a grid of spacing $2\pi \times 0.02$ Å^{-1}. The forces on atoms are converged to less than 10^{-3} eV/Å. Phonon spectra were computed using the PHONOPY code that is interfaced with VASP gamma point density functional perturbation theory (DFPT).[25] The crystal structures are plotted using the VESTA program,[26] and the space groups were identified using FINDSYM[27] and Spglib.[28]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Cyclohexadiene and cyclobutane models for the 3D structure. Calculated XRD patterns of *squaroglitter*, graphite, and diamond, and the product of cold compressed graphite. A detailed analysis of orbital contributions around the Fermi level. The electronic structure of some metal-threaded networks (PdC$_4$). A mixed carbon—boron squaroglitter. Optimized crystallographic information of *squaroglitter*. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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