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A Hypothetical Metallic Allotrope of Carbon

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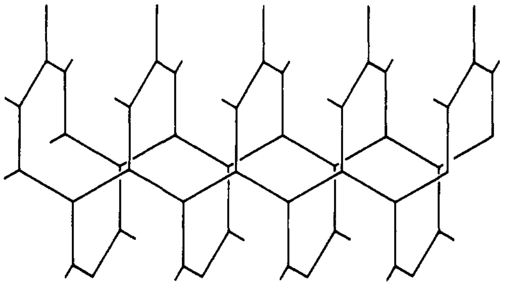
Graphite is not the only way to fill space with trigonal sp^2 carbon atoms.[1] *Many* three-dimensional trigonal networks can be constructed,[2-5a] varying in density and in degree of conjugation. One of the most intriguing ones is **1**. This is the $ThSi_2$ structure, found in a number of other materials as well.[5b]



1

In **1** there are infinite polyene chains (no assumption made as yet concerning bond localization within each chain) running along two dimensions and no conjugation along the third dimension. While the network is free from angle strain, it is not free from "π-strain". The π-clouds of neighboring polyenes are much too close together. If a CC distance of 1.44 Å within a polyene is assumed, then the perpendicular distance between polyene chains is 2.494 Å, far from comfortable from what we know about π-systems impacting on each other.[6] However, it is just this enforced proximity of the π-clouds of the polyene chains that is going to make **1** metallic.

The density of **1** is an attractive 2.97 g cm^{-3}, assuming CC 1.44 Å. This is close to diamond and graphite, 3.51 and 2.27 g cm^{-3}, respectively.[7] The smallest rings in **1** contain 10 and 12 carbons. The network has an interesting deformation available to it, the result of rotating around all the "vertical" bonds. This leaves all CCC angles at 120°, increases the density, but brings the polyenes still closer together. The space group of **1** is $I4_1/amd$, with eight atoms in the unit cell.

The band structure of **1**, approximated by an extended Hückel[8] calculation, is shown in Figure 1, along with the calculated density of states. The obvious feature is that of bands of high dispersion. The Fermi level at −9.9 eV cuts several of these bands.[9] The material appears metallic with substantial density of states at the Fermi level.[10] As would be expected from the absence of π-conjugation along the vertical direction in **1**, there is a large gap along the corresponding line Γ(v)M in the band structure.

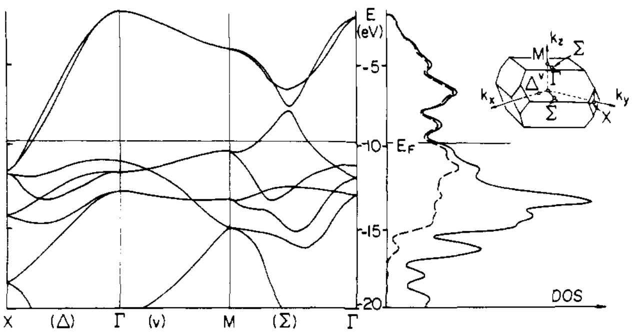
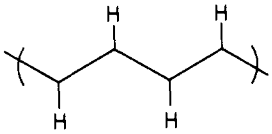


Figure 1. Energy band structure and density of states of **1**. The dotted line corresponds to the "polyenic" π-electron projected density of states. The inset shows the labeling of the high-symmetry points in the Brillouin zone.[12]

Is the high dispersion of the energy bands due to conjugation within the polyene chains or to the mutual overlap of neighboring chains? This question is traced by examining a progression of structures of intermediate complexity: **2**, a single polyene chain, $(CH)_x$; **3**, two such chains, parallel, 2.494 Å apart; **4**, an infinite array of such parallel chains; **5**, a two-dimensional model for **1**.



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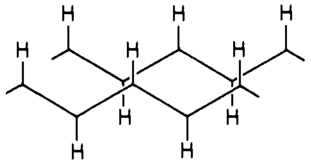

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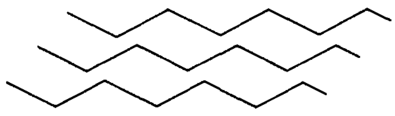

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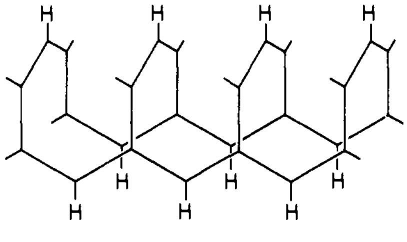

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The band structure of polyacetylene or polyene, **2**, is well-known,[11a] as is its propensity for bond alternation.[11b] The large

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[1] Balaban, A. T.; Rentia, C. C.; Ciupitu, E. *Rev. Roum. Chim.* **1968**, *13*, 231–247. This reference contains a detailed discussion of sheets of trigonal carbon where the angles deviate from 120°.

[2] Gibson, J.; Holohan, M.; Riley, H. L. *J. Chem. Soc.* **1946**, 456–461. Riley, H. L. *J. Chim. Phys.* **1950**, *47*, 565–572.

[3] Eisenstein, O.; Hoffmann, R.; Balaban, A. T. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 5588–5592. This hints at some.

[4] Nikerov, M. V.; Bochvar, D. A.; Stankevich, I. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 1177–1178; *Zh. Strukt. Khim.* **1982**, *23*, 1, 177–179; **1982**, *23*, 4, 13–19; **1982**, *23*, 5, 16–20. See also: Matyushenko, N. N.; Strelnitsky, V. E.; Gusev, V. A. *Kristallografia* **1981**, *26*, 484–487.

[5] (a) Wells, A. F. "Three-Dimensional Nets and Polyhedra"; Wiley: New York 1977. (b) Pearson, W. B. "The Crystal Chemistry and Physics of Metals and Alloys"; Wiley-Interscience: New York, 1972; pp 518–520. A recent interesting example of this structure type is LaPtSi: Klepp, K.; Parthé, E. *Acta Crystallogr., Sect. B* **1982**, *B38*, 1105–1108.

[6] In cyclophanes two benzene rings are forced to 2.6–3.0 Å of each other by bridges, and they show clearly in their structures that the aromatic ring is deformed substantially by this close approach. See for the relevant references: Boekelheide, V. *Acc. Chem. Res.* **1980**, *13*, 65–70. Naphthalenes disubstituted in the 1,8-positions by π-systems create a geometry analogous to ours, and deformations indicative of repulsion are clearly seen; inter alia see: House, H. O.; Koepsell, D. G.; Campbell, W. J. *J. Org. Chem.* **1972**, *37*, 1003–1011. Avoyan, R. L.; Kitaigorodskii, A. I.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1963**, *4*, 633–636; **1964**, *5*, 421–439.

[7] These are idealized theoretical densities. Real samples of graphite and diamond have lower densities.

[8] A leading reference for extended Hückel band calculations is given in the following: Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 6093–6098.

[9] Extended Hückel calculations will place the Fermi level too low. The actual work function should be 3–5 eV less in magnitude.

[10] There is a substantial literature on the possibility of a metallic form of carbon under high pressure. The structure(s) in question are very different from this one. See for a leading reference: Bundy, F. P. *J. Geophys. Res.* **1980**, *85*, 6930–6936.

[11] (a) Kertész. M. *Adv. Quantum Chem.* **1982**, *15*, 161–214 and references therein. (b) Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc. London, Ser. A* **1959**, *A251*, 172–185.

[12] See, e.g.: Lax, M. "Symmetry Principles in Solid State and Molecular Physics"; Wiley: New York, 1974; pp 449. M(Σ)Γ indicates an alternative pathway to Γ(v)M between these two special points. Due to crystal symmetry the continuation of the Σ line connects two faces of the Brillouin zone.

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p–p π overlap leads to a half-filled, folded-back π-band of total width 8.64 eV, with the Fermi level at −10.85 eV. This is for equal, nonalternating CC of 1.44 Å. When two such chains are brought together to 2.494 Å, as in **3**, they naturally repel each other. Paired polyene levels split by $\sim$2 eV. Interestingly, the overlap of the bands results in a density of states that suggests metallic behavior even for this two-chain model. In **4** the band width due to interchain p–p σ overlap is $\sim$4 eV, comparable to the dispersion due to p–p π overlap within one chain. In **5** and in the complete structure **1** it becomes difficult to separate the sources for the high dispersion, but clearly both inter- and intrachain overlaps contribute.

It is interesting to examine the nonbonded (2.494 Å) CC overlap population. It changes from −0.002 in **3** to +0.04 in **4**, to +0.06 in **5**, and to +0.013 in **1**. Note the positive values. Perhaps one way to think about this is that in some segments of the Brillouin zone one has gone past the repulsive region of interchain π-cloud interaction into the attractive regime of σ-bond formation between chains.

Further numerical experiments show that (1) the network in **1** resists the twisting deformation; (2) bond localization within the polyenes does not lead to an opening of a gap at the Fermi level or to net stabilization in **1**, **3**, **4**, or **5**; (3) from geometry optimization we expect the CC distance in **1** to be intermediate between graphite and diamond, and vertical nonconjugated bonds should be longer than the polyenic ones; (4) the computed total energy of **1** is −70.26 eV/C compared to −71.00 eV/C for graphite. These numbers are subject to the unreliability of the extended Hückel method. That the hypothetical structure **1** is unstable with respect to graphite is not a barrier to its existence—most molecules are thermodynamically unstable with respect to the elements but exist because of large kinetic barriers to geometrical transformation which break bonds. Many such bonds would have to be broken, at large cost in energy, in order to transform **1** to graphite.

Can this metallic form of elemental carbon, or other alternative structures, be synthesized?

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Mechanisms of Water Oxidation to Oxygen: Cobalt(IV) as an Intermediate in the Aquocobalt(II)-Catalyzed Reaction

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Both heterogeneous and homogeneous catalyses of water oxidation to O_2 have been recently reported for metal oxides[1] and aquo- or hydroxo-metal complexes.[2] One of the more efficient systems involves cobalt(II) catalysis of water oxidation by $\mathrm{Ru(bpy)_3}^{3+}$ ($E°(\mathrm{Ru(bpy)_3}^{3+/2+}) = 1.26$ V), which occurs above pH $\sim$5[2a] (eq 1). We have studied the kinetics and product distribution of this system at pH $\sim$7 (at pH 7, $E°(O_2/H_2O_2) = 0.27$ V, $E°(H_2O_2/H_2O) = 1.36$ V). Although the kinetic behavior is extremely complicated in both the absence[3] and presence[4] of Co(II), our results provide compelling evidence for rate-determining formation of a Co(IV) species that reacts with water or hydroxide ion to produce H_2O_2, with regeneration of the catalyst Co(II).

$$\mathrm{Ru(bpy)_3}^{3+} + {}^1/_2\mathrm{H_2O} = \mathrm{Ru(bpy)_3}^{2+} + \mathrm{H^+} + {}^1/_4\mathrm{O_2} \quad (1)$$

As reported by Shafirovich et al.,[2a] O_2 formation according to eq 1 is stoichiometric at pH $\sim$7 when the initial $[\mathrm{Ru(bpy)_3}^{3+}]$ is $\sim$10[Co(II)].[5] Consistent with this we find that the rate of $\mathrm{Ru(bpy)_3}^{2+}$ formation is greatly accelerated by the addition of Co(II). In the presence of Co(II), added Ru(II) markedly slows the rate,[6] establishing that product inhibition is a factor, and the absorbance–time behavior with excess Ru(II) manifests a second-order Ru(III) dependence. Over the range [Ru(III)] = $(0.01\text{–}1.5) \times 10^{-3}$ M, [Co(II)] = $(1\text{–}60) \times 10^{-6}$ M with added Ru(II) ≤ 10[Ru(III)] and [Ru(III)] ≥ 10[Co(II)], the fits to a second-order Ru(III) dependence are excellent and the second-order k_{obsd} is inversely proportional to [Ru(II)].

The rate exhibited a complex [Co(II)] dependence. With $(0.3\text{–}1.0) \times 10^{-3}$ M Ru(III) the value of k_{obsd}[Ru(II)] decreased with increasing initial [Ru(III)] at a given [Co(II)] and plots of k_{obsd}[Ru(II)] vs. [Co(II)] curved upward. Such behavior suggests catalyst deactivation. Since the initial [Ru(III)] was 10–100 times greater than the added [Co(II)], the diversion of a small fraction of the cobalt catalyst per catalytic cycle (to, for example, an inactive Co(III) dimer or polymer) could lower k_{obsd}[Ru(II)] when [Ru(III)] is increased at constant [Co(II)]. In an attempt to simplify the behavior in the high Ru(III) region, the kinetics of the reaction of equimolar Ru(III) and Co(II) were studied by the stopped-flow technique. Drastically different absorbance–time profiles were, however, observed: the reaction exhibited triphasic behavior with most of the Ru(II) (450 nm) being produced in a rapid, apparently zero-order stage. Intense transient absorption at $\sim$600 nm obscured the Ru(III) disappearance normally monitored at 675 nm, and a black solid containing >90% of the cobalt precipitated from the product solutions. Thus Co_2O_3 or a related solid is produced when [Ru(III)] and [Co(II)] are comparable and leads to the greatly diminished O_2 yield[2a,5] under these conditions.

Because of the complications described above, measurements were extended to lower Ru(III) and Co(II) concentrations. At pH 6.5–7.2 (0.025 M phosphate, 0.1 M ionic strength, 25 °C) with $(1\text{–}10) \times 10^{-5}$ M Ru(III), $(1\text{–}10) \times 10^{-4}$ M Ru(II), and $(1\text{–}6) \times 10^{-6}$ M Co(II),[7a] the rate law for disappearance of $\mathrm{Ru(bpy)_3}^{3+}$ is given by $-d[\mathrm{Ru(III)}]/dt = a[\mathrm{Ru(III)}]^2[\mathrm{Co(II)}]/[\mathrm{Ru(II)}][\mathrm{H^+}]^2$ with $a = (4 \pm 1) \times 10^{-10}$ M s^{-1}. The rate is first order in [Co(II)], inverse second-order in [H$^+$], and, as before, second order in [Ru(III)] and inverse in [Ru(II)], but in this region, a is constant over a factor of 10 range in [Ru(III)], and Co_2O_3 formation is not observed.[7b] The rate law implicates a scheme such as eq 2–5

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(1) Kiwi, J.; Grätzel, M. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 860. Lehn, J. M.; Sauvage, J. P.; Ziessel, R. *Nouv. J. Chim.* **1980**, *4*, 355. Kiwi, J.; Kalyanasundaram, K.; Grätzel, M. *Struct. Bonding* (*Berlin*) **1982**, *49*, 37.

(2) (a) Shafirovich, V. Ya.; Khannanov, N. K.; Strelets, V. V. *Nouv. J. Chim.* **1980**, *4*, 81. (b) Harriman, A.; Porter, G.; Walters, P. *J. Chem. Soc., Faraday Trans.* **1981**, *2*, 2373. (c) Gersten, S. W.; Samuels, G. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4029. (d) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *J. Chem. Soc., Chem. Commun.* **1982**, 1288.

(3) Creutz, C.; Sutin, N. *Proc. Natl. Acad. Sci. U.S.A* **1975**, *72*, 2858.

(4) Ghosh, P.; Brunschwig, B. S.; Chou, M. H.; Creutz, C.; Sutin, N., manuscript in preparation.

(5) Oxygen yields were determined by gas chromatography (Ar or He carrier, 2 m × 0.3 cm molecular sieve 5A column) of the gas phase above $\mathrm{Ru(bpy)_3}^{3+}$ solutions (pH 7, 0.025–0.25 M phosphate) reacted at $\sim$22 °C. With 1.0×10^{-3} M Ru(III) the following yields were obtained (−log [Co(II)] added as $CoSO_4$, percent O_2 based on eq 1): 6.7, 10; 5.7, 28; 4.6, 68; 4.3, 95; 4.0, 95; 3.7, 66; 3.4, 55; 3.2, 18. The yield profile, which features a maximum O_2 yield between 5×10^{-5} and 3×10^{-4} M Co(II), is in excellent agreement with that reported in ref 2a. With lower initial [Ru(III)] the maximum yield shifts to lower [Co(II)]. At 2.0×10^{-4} M Ru(III) the maximum O_2 yield is near 1×10^{-5} M Co(II) (−log [Co(II)], percent O_2 in 0.025 M phosphate at pH 7): 6, 68; 5, 98;, 4.3, 83. In the absence of Co(II), ≪10% O_2 was found; instead, $\mathrm{Ru(bpy)_3}^{2+}$ formation (in >90% yield) was accompanied by the formation of CO_2 and Ru(II) complexes containing partially oxidized bpy ligands.[4] In Co(II)-containing solutions the yields of these ligand-oxidized products dropped as the O_2 yield increased.

(6) Note that in the absence of Co(II), the Ru(III) decay *accelerates* in the presence of $\mathrm{Ru(bpy)_3}^{2+}$ and with initial [Ru(III)].[3,4].

(7) (a) These data were determined for argon-saturated solutions. (b) After the completion of the kinetic runs, the solutions were subjected to Millipore filtration, and their cobalt content was determined by atomic absorption: >90% of the cobalt originally added was present in the filtrate.

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