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Potentially Conducting Organometallic Systems: The Stibaphenalenyl Series

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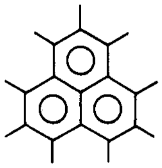
Substituting some carbon atoms by antimony in the network of the odd alternant hydrocarbon phenalenyl ($C_{13}H_9$) radical can lead to a variety of new molecules. These molecules are investigated theoretically by using extended Hückel computations, which point to a high potential of the compounds to be good organometallic conductors. Two main features are characteristic of all the members of the series: (a) the molecules exhibit an inherent propensity to form infinite stacks that are driven by strong intermolecular Sb- - -Sb bonding, and (b) the band structure of the stacks exhibits a few bands that are all less than half-filled. Each such band, by itself, may be conceived to arise from stacking of partially oxidized (doped) donors. The stibaphenalenyl stacks meet thereby the two main requirements of the highly conducting organic "metals".

There exist two broad classes of organic conductors.[1] The first class contains segregated stacks of organic donors (D) and acceptors (A), such as the now celebrated TTF·TCNQ. The second class consists of salts of organic D's or A's, such as the superconducting Bechgaard and ET salts[1d,e] $(TMTSF)_2ClO_4$ and $(ET)_2I_3$. All the presently known organic "metals" and superconductors have two common features, which are also necessary conditions for high conductivity. One condition is electronic and requires the existence of an organic molecule with an average nonintegral charge.[1b] The other condition is architectural and requires more or less[1d,e] stacking of like molecules (D or A) that overlap sufficiently strongly to create an electronic band and thereby a "spine" for conductivity. The search for new types of organic conductors is as ever intense[1g,h] and promises to retain the vitality of this exciting interdisciplinary field.

About 10 years ago, Haddon[2] pointed out the potentiality of odd alternant hydrocarbons (and especially phenalenyl (**1**)) as novel conducting systems. Although these materials looked very promising on several grounds, the initial expectation has as yet not been realized. As part of our continuing interest in the design of novel systems with interesting physical or chemical properties,[3] we report here an approach that may help to realize the potential of **1**. The approach relies on the introduction of a group 15 atom, like Sb, into the phenalenyl skeleton (**1**).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Although only nitrogen or boron atoms have been introduced to date into the phenalenyl network,[4] the introduction of antimony may be feasible too in view of its introduction into some cyclic conjugated systems.[5] As we reason in what follows, the introduction of Sb seems to provide the two necessary conditions: (a) a driving force for stacking and (b) an electronic effect that is equivalent to nonintegrally oxidizing or reducing each molecule in a stack. Both these conditions do not require—to be met—the counterpart molecule, be it an acceptor or an anion. Our base reasonings are later supported by extended Hückel tight-binding calculations whose details are outlined in the Appendix. Hereafter the proposed systems will be referred to by the general name "stibaphenalenyl", which signifies the skeleton of **1** with any given number of Sb atoms substituting C–H vertices.

Base Reasonings

Our interest in the above systems was initiated by several observations. First, antimony compounds are known to possess a propensity to stack in the solid state, and the stacks contain relatively short Sb- - -Sb distances.[5b,6] This is the origin of the thermochromic effect exhibited by distibines.[5b,6,7] Second, the introduction of a group 15 element (X = N, P, As, Sb) into the benzene ring was shown to lead to a progressive decrease of the HOMO–LUMO gap as the size of X increased from N toward Sb.[8] This decrease of the HOMO–LUMO gap is likely to intensify the intermolecular HOMO–LUMO interactions between two stibaphenalenyl molecules. The above two observations together suggest that, if made, the stibaphenalenyl molecules should favor stack formation with possibly an Sb-over-Sb arrangement;[5–8] the architectural condition for conductivity will thereby be met. Third, Sb possesses diffuse p orbitals, which will form, upon stacking of stibaphenalenyl, wide energy bands. Owing to their width, these bands are likely to cross several other bands, e.g. carbon-centered bands, which are *narrow* and which are generated from *filled molecular orbitals* of stibaphenalenyl. Such crossings will result in several partially filled bands. This feature may endow the stibaphenalenyl solids with a metallic behavior. Thus, the

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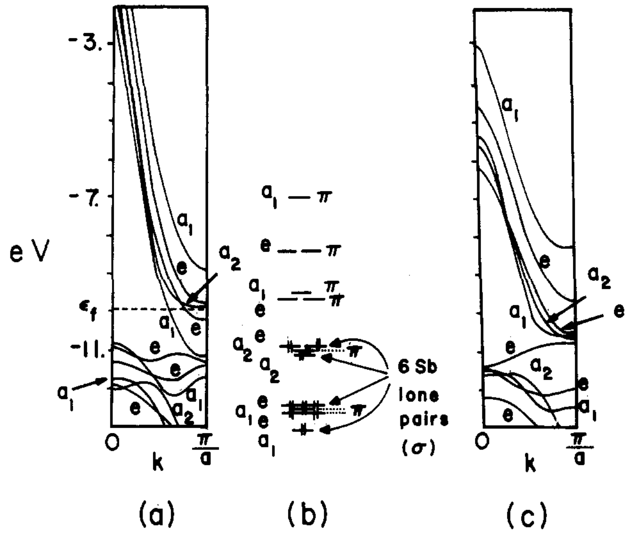


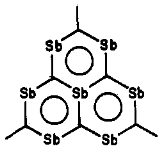
Figure 1. Band structure for stack 3 with d = 3.22 Å (a) and d = 3.62 Å (c). Also shown are the energy levels for the monomer 2 (b).

electronic condition for conductivity (vide supra) may be met without the need of a counterion or an acceptor counterpart molecule.[1j]

These base reasonings, in addition to the features discussed by Haddon,[2] directed our attention to the phenalenyl network substituted with Sb atoms. In dealing with the problem of replacing certain atoms in a given homonuclear network, the simplest method to predict the most stable arrangement is to perform a calculation on the parent network and to reserve the most negatively charged sites for the more electronegative atom.[9] Antimony and carbon have a very similar electronegativity, and hence, it is expected that there will not be a strong positional preference. This endows a considerable flexibility to the type of systems chosen here.

Extended Hückel Band Calculations

Although the above arguments suggest that derivatives of phenalenyl, such as the heptastiba compound 2, could be an organic metal, it is eventually imperative to test the main points of the reasoning by detailed computations. The system $C_6Sb_7H_3$ (2), which we choose to inspect in detail, is a closed-shell molecule as any centrally substituted stibaphenalenyl. The band structures of a perfect stack 3 at two different intermolecular distances, 3.22 and 3.62 Å, are shown in Figure 1 along with the MO levels of the isolated molecule. The distance 3.62 Å corresponds to the long Sb–Sb distance in the 2,2′,5,5′-tetramethylbistibole solid-state polymer 4, while 3.22 Å, which is the mean value between the long and short distances in 4, coincides with the optimized intermolecular distance of the stack 3.



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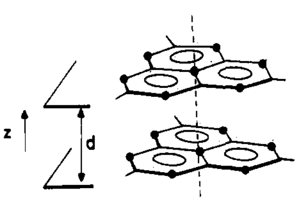

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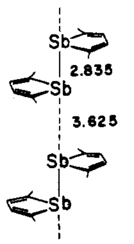

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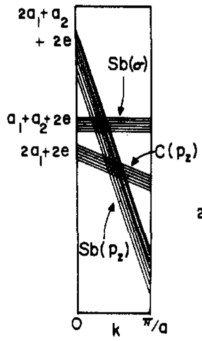
At 3.22 Å the stack is calculated to be 1.95 eV/unit more stable than the isolated molecule. A sizable stabilization still remains at 3.62 Å. Although in absolute value the stabilization energy may be overestimated, the results clearly unravel a strong propensity toward stacking. Let us then proceed to look in some detail at the band structure of 3. Note that the band structures at 3.22 and 3.62 Å are qualitatively very similar, with seven very dispersive bands mainly Sb-centered.

The band structure of extended systems is usually analyzed in terms of the molecular orbitals of the unit cell,[10] but owing to the large stacking interaction in 3, the molecular approach is not the most lucid description in this case. The bands near the Fermi level are those derived from the π-type p_z orbitals of Sb and C and the six σ-type in-plane Sb lone pairs. Since the Sb and C atoms alternate along the skeleton, we can consider separately the orbitals of the two atomic types as shown in 5. From the six carbon p_z orbitals we can form six bands which at 3.22 Å will have a dispersion of about 1 eV.[11] These bands in 5 possess the symmetries $2a_1 + 2e$ corresponding to the C_{3v} group, which is the appropriate one for all k points other than 0 and π/a. From the seven Sb p_z orbitals we can form seven bands that, due to the large Sb–Sb overlap, are very wide and whose symmetries are $2a_1 + 2e + a_2$ (5). To these π-type bands we should add six completely flat bands representing the σ lone pairs of the circumferential Sb atoms. These bands are of symmetries $a_1 + a_2 + 2e$. As a result of the strong Sb–Sb interaction, the seven Sb(p_z) bands intend to cross both the C(p_z) and the Sb(σ) bands, as shown in 5. These three zero-order bands interact and, by avoided crossings, generate the band structure of Figure 1.



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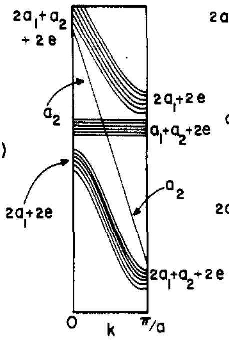
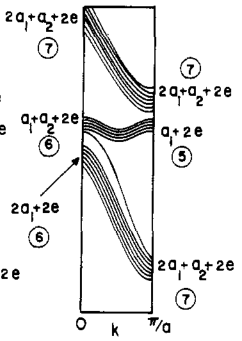


6a



6b

The avoided crossings are illustrated in two steps, in **6a**,**b**. A strong avoided crossing between Sb(p_z) and C(p_z) generates the six lower bands $2a_1 + 2e$ in **6a**. Simultaneously, six bands ($2a_1 + 2e$) are pushded high up in energy due to the same avoided crossing. The seventh Sb(p_z) band, of a_2 symmetry, does not find at this stage a symmetry match among the C(p_z) band, and therefore, the a_2 band remains as originally, a wide band cutting across diagram **6a**. In the second step in **6b**, we consider the weak interaction of the Sb(σ) bands ($a_1 + a_2 + 2e$) with the presently upper bundle of mixed Sb(p_z)–C(p_z) bands and with the a_2 Sb(p_z) band. As a consequence of this interaction the Sb(σ) band acquires a belly, while the a_2 Sb(p_z) and a_2 Sb(σ) bands avoid their crossing. The result in **6b** is that at $k = \pi/a$, the a_2 band joins the upper bundle, which now contains seven bands, leaving five bands at the middle bundle, as indicated by circled numbers in **6b**. Thus the final band structure of heptastibaphenalenyl (2) should look like **6b**, which qualitatively mimicks the calculated band structure in Figure 1 (note that Figure 1 does not show the lower bundle of bands all the way to their energies at $k = \pi/a$). We now understand the results of the calculations on quite a fundamental basis.

Let us turn to the band occupation. There are 12 lone-pair electrons and 14 π electrons to be placed into the bands of **6b**.

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(9) Gimarc, B. M. *J. Am. Chem. Soc.* **1983**, *105*, 1979.

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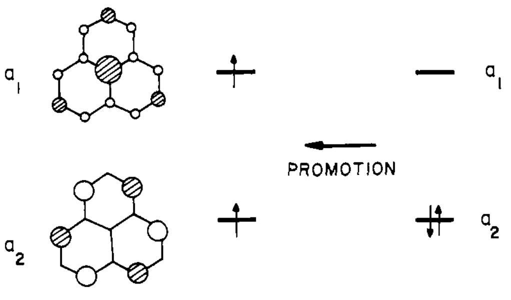
(11) Whangbo, M.-H.; Stewart, K. R. *Isr. J. Chem.* **1983**, *23*, 133. Canadell, E.; Alvarez S. *Inorg. Chem.* **1984**, *23*, 573.

This requires 13 filled bands, so that two electrons end up being distributed among the band orbitals of the upper bundle. The result is that at the Fermi level there exist a few partially (less than half) filled bands. With this type of fractional band filling (see Figure 1a), dimerization is not possible and trimerization or tetramerization is very unlikely. The system should then be metallic. Strictly speaking, in view of the one-dimensionality of the stack in our calculations, it will be susceptible to incommensurate charge density wave (CDW) instabilities at low temperatures.

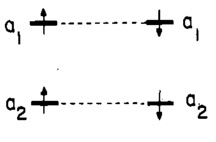
A. Why Does Stibaphenalenyl Tend To Stack? The qualitative analysis of the actual band structures, using AOs rather the MOs of the molecular unit, not only is a matter of pedagogy but pinpoints the crucial feature of these stacks: the molecule has lost its electronic integrity. Put differently, there is an important electronic reorganization under stacking, such that the stack of the heptastibaphenalenyl may be thought of as a bundle of seven Sb chains held together by six carbon atoms in a local phenalenyl network. This loss of the electronic identity of the molecular unit is manifested by the several partially filled bands in Figure 1. Thus each band, *by itself*, may be conceived to originate from nonintegral charging of an initially closed-shell molecule in a stack.

The electronic reorganization of heptastibaphenalenyl can be projected by inspection of the molecular orbital occupation of a molecule in the stack of Figure 1. The same information can be obtained by looking at a dimer of heptastibaphenalenyl. At a distance of 3.22 Å each molecule, in the dimer, is approximately represented by an electronic configuration that involves single-electron occupation in the a_2 and a_1 orbitals as shown in **7a**, the rest of the orbitals being either doubly occupied or vacant (approximately). This means that, relative to the ground state **7b**, the molecule in the dimer (or stack) undergoes electronic promotion from the π-type HOMO (a_2) to a π-type vacant orbital (a_1), which possesses nearly the same energy as the π-LUMOs (e-type orbitals; see Figure 1).



7a **7b**

Pairing up of the odd electrons, **7a**, across the molecules of the dimer generates two bond pairs between the molecules as shown in **8a**. The bond pairs, which are of the a_1–a_1 and a_2–a_2 varieties, involve predominantly Sb- - -Sb interactions because (a) the a_2 orbital is a pure Sb orbital, while the a_1 orbital is more heavily centered on the Sb atoms, and (b) the Sb- - -Sb overlap is overwhelmingly larger than the C- - -C overlap.



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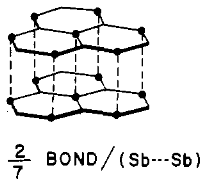

8b

The intermolecular bonding is shown pictorially in **8b** and corresponds to approximately two-sevenths of a bond between each Sb- - -Sb pair. We may then conclude that in the stack, there exist seven $(Sb)_\infty$ chains, each of maintaining approximately one-seventh of a bond between successive Sb atoms. The EH computations reveal indeed a large positive Sb- - -Sb overlap population (~0.2 at 3.22 Å) and a very small and negative C- - -C overlap population (−0.03 at 3.22 Å).

To summarize: the molecules in the stack undergo electron unpairing, and thereby they loose *intramolecular* bonding only to regain stronger *intermolecular* bonding. There is though a problem in the argument because the above process involves a balance between the intramolecular promotion energy (**7b** → **7a**) and the intermolecular bonding energy. We have to verify, then, that intermolecular bonding can overcome the promotion energy of heptastibaphenalenyl.

The promotion energy of stibaphenalenyl (**7b** → **7a**) corresponds approximately to a singlet to triplet excitation ($a_2 \rightarrow a_1$). Experimental excitation energies[4b,g,12] are ~40 kcal/mol for azaphenalenyl derivatives. The corresponding value for the Sb compound should be significantly lower, in view of the results of Ashe et al.[8] that show shrinkage of the HOMO–LUMO energy gap upon substitution of N by Sb. Thus, to begin with, the promotion energy of heptastibaphenalenyl should be quite a small quantity, significantly smaller than 40 kcal/mol.

A reasonable measure for the intermolecular bonding is the Sb–Sb bond energy, which is ~39 kcal/mol.[13] Since there is an average of one Sb–Sb bond per molecule in a stack of heptastibaphenalenyl (see **8b**), we may estimate the strength of the intermolecular bonding at ~39 kcal/mol. It seems reasonable then that the intermolecular bonding energy can override the promotion energy of heptastibaphenalenyl. The stacking of this molecule appears thus "to pay more than its cost".

We have made one additional test. One might have argued that the computational results, in Figure 1, are the way they are because we have used Sb orbitals that are very diffuse, with artificially too large an overlap. To counter this argument, we have repeated the calculations with contracted orbitals, those of tellurium,[14] which represent an upper limit contraction for Sb. The resulting band structure is still equivalent to Figure 1, with 0.85 eV/molecule of stacking energy gain and strong Sb- - -Sb bonding. Thus, it is not the diffuseness of the Sb orbitals or some other artifact that dictates the computational result. These seem to derive from the topology of the molecule, which due to its peripheral [12]annulenic skeleton possesses inherently a small HOMO–LUMO gap that is further diminished by Sb. There results thereby a low promotion energy (**7b** → **7a**). It is thus the odd alternant structure of stibaphenalenyl that endows this compound with the driving force to stack.

The above arguments make the computational results chemically plausible. It is likely, then, that if the Sb compound can be made, it will stack and exhibit a metallic state resulting from a band structure like that shown in Figure 1. It is thus possible to obtain partially filled stacks from closed-shell molecules without having to oxidize or reduce them either chemically or electrochemically.

There is one caveat: the small HOMO–LUMO gap will also render the molecule kinetically unstable.[5-7] Some care may be taken then to ensure that the stacking of stibaphenalenyl will compete favorably with its other side reactions.

B. The Best Stacking Mode of Stibaphenalenyl. Having rationalized the computational results, we should worry about possible slipping motions that would destroy the perfect stacking considered so far. We have studied two slipping motions schematically shown in **9**. In the first case we start with seven Sb–Sb contacts, and by slipping we end up with two contacts (**10**). In the second case we end up with four Sb–Sb contacts (**11**). In both cases we have optimized the intermolecular distance for each value of the slipping parameter δ. The relative energy values for **3** (seven Sb–Sb), **11** (four Sb–Sb), **10** (two Sb–Sb), and the isolated molecule are 0.0, 1.0, 1.3, and 1.9 eV, respectively. Although these numerical values should not be taken quantitatively, they clearly reflect the number of Sb contacts. In all cases there are important

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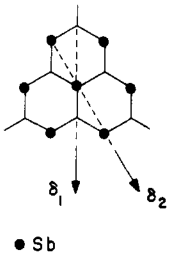
(12) Leupin, W.; Wirz, J. *J. Am. Chem. Soc.* **1980**, *102*, 6068.

(13) Sanderson, R. T. *Polar-Covalence*; Academic: New York, 1983; p 41.

(14) $\zeta_{5s} = 2.51$ and $\zeta_{5p} = 2.16$. See: Bernstein, J.; Hoffmann, R. *Inorg. Chem.* **1985**, *24*, 4100.



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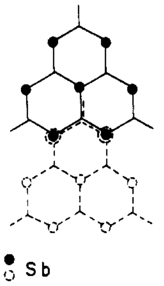

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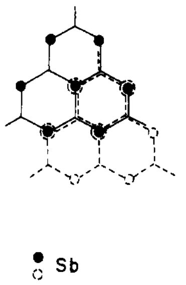

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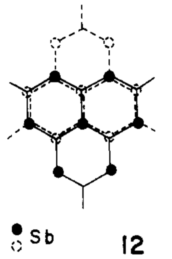
barriers along the slipping motion which prove that the Sb–Sb interactions overwhelmingly dominate the energetics of the stacking.

In order to probe in more detail the competition between "Sb–Sb" and "Sb–C" stacking, we have compared **3** with the ultimate case for "Sb–C" contacts, i.e., a stacking **12**, which contains 10 such Sb–C chains. The chain **12** was found to be unstable toward dissociation. We conclude therefore that heptastibaphenalenyl will have a strong tendency to stack in the form **3**. The only alternative form should be **13**, which contains seven Sb–Sb contacts in a staggered ring–ring relation (by 60°). We calculate this staggered stack to be only slightly more stable (0.18 eV/unit) than **3** so that both types of stacking are likely to be found. Since the Sb–Sb contacts are identical in both chains, the band structures are equivalent.[15]



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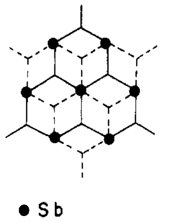

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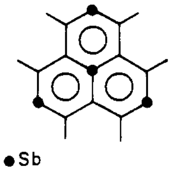
It is worth noting that partial oxidation or reduction of the molecular stacks, **3**, should not alter the gross electronic features of the material. A tuning of the occupation of the dispersive higher bands by cocrystallization with other organic/inorganic materials could nevertheless lead to some interesting salts.

The Stibaphenalenyl Series

It is not our purpose to go in detail through the different possibilities of Sb substitution for C in the phenalenyl network, but only to point out some interesting features offered by this strategy. The principles are simple and resemble the process outlined in **5** → **6**. Thus, for *n* antimony atoms in the network, there will be *n* wide Sb(p_z) bands that will be crossed by *n* (or $n - 1$ if the central atom on the network is Sb) flat Sb(σ) lone-pair bands and $13 - n$ fairly flat bands, which are descendents of the C p_z orbitals. These latter bands may come in one or a few bundles, depending on whether the Sb atoms segregate the carbon atoms or not. The avoided crossings of the zero-order bands will usually lead to a few bands that are less than half-filled, as in the heptastibaphenalenyl.

Let us briefly consider **14**. This is again a closed-shell molecule.



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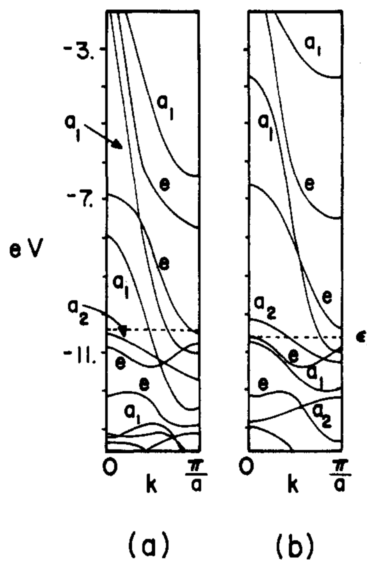
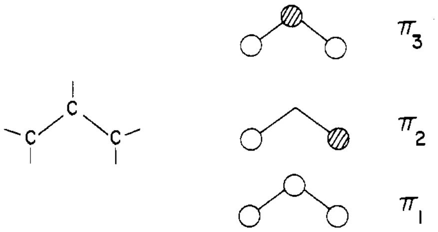
There exists now a possibility of forming four Sb "chains" along with a marked tendency to stack via Sb–Sb bonding. Indeed, at 3.22 Å we calculate an energy stabilization of 0.91 eV/unit with respect to the isolated molecule. It is easy to show that this system should also have a series of partially filled bands.



(a) (b)

Figure 2. Band structures for the eclipsed one-dimensional stacks of **14** (a) and **17** (b) with an intermolecular distance of 3.22 Å.

Let us construct a schematic band structure as we did for **3**. Since there are four antimony chains, we form four Sb(p_z) wide energy bands of symmetries $2a_1 + e$. The flat Sb(σ) lone-pair bands are of symmetries $a_1 + e$. The C(p_z) bands cannot be constructed individually for each carbon "chain" because now there exist C–C contacts within the basic molecular unit. Instead, the bands should be constructed from the orbitals of the three allylic carbon fragments of **14**. These fragment MOs are shown in **15**.



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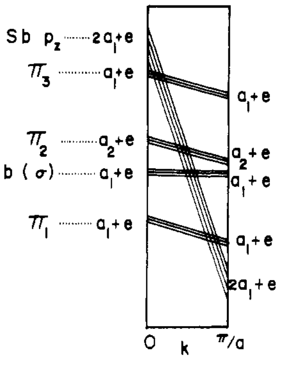
From π_1 and π_3 we generate two bundles of three bands each with symmetries $a_1 + e$, as shown in **16**. The two bundles are separated by the initial π_1–π_3 energy gap. From π_2 we can generate three bands of symmetries $a_2 + e$ lying between the two former bundles. The final band structure can be obtained, as before, by consideration of the different avoided crossings. Part of this band structure is shown in Figure 2a. Nevertheless, we do not need to go into all these details. Having 14 π electrons and 6 lone-pair electrons, we have to occupy 10 of these bands, which means that 2 electrons should go into the wide Sb bands ($2a_1 + e$). These bands intend to cross the third bundle of flat bands near π/a. The system is then electronically equivalent to **3**, and the previous conclusions should apply.



16

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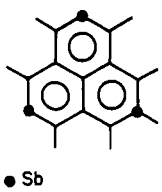
[15] Apart from the doubling of the bands, the only change is that the lower set of bands in **5** should be completely flat instead of somewhat dispersive.

It is interesting to look also at the systems that are devoid of a central Sb atom, **17** and **18**. These are the open-shell counterparts of the systems examined above. The radical **17** possesses an odd electron in the nonbonding orbital **19**. Since the odd electron is exclusively on the carbon atoms, recombination of successive radicals into C–C bonds would require that the stacking distance can become considerably short. However, this distance is determined exclusively by the Sb- - -Sb interactions and cannot be much shorter than ~3 Å. At such a long distance the radical-pairing interaction is too small to cause dimerization. The band structure should be very similar to **16**. The only difference is that now one of the wide a_1 $\mathrm{Sb}(p_z)$ bands disappears and a new carbon-based a_1 band appears in the central part of the diagram, **20**.[16] After avoided crossings, the e component of the middle bundle in **20** will be stabilized while the a_2 band will remain at its original energy. There will then exist nine bands that are lower in energy than a_2. Since there is a total of 19 π and lone-pair electrons, the a_2 band will end up being partially filled.



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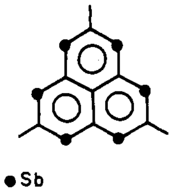

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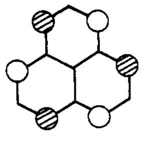

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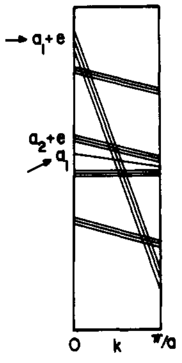
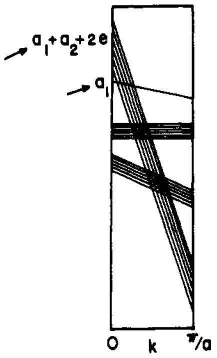


20

The resulting band structure at 3.22 Å, is shown in Figure 2b. At this distance, the Sb-centered a_1 + e bands descend low enough to be slightly populated. The result is that a_2 will be less than half-filled. At larger distances, the a_1 + e bands will not descend low enough to be populated, and the a_2 band will be half-filled. Since the a_2 band is quite flat and will get flatter at longer distances, the second situation will most likely correspond to a magnetic insulator (flat bands lead to electron localization). On the other hand, the first situation, if realized, will correspond to a metallic material, owing to the partial population of the wide a_1 and e bands (Figure 2b). The material may be fluxional enough to be able to transit from one situation to the other. This can be a very interesting material.

18 is also a radical with an electron in the a_2 orbital **19**. Since this orbital is now antimony-based it should certainly be an ideal system to stack. The schematic band structure will be that of the centrally substituted compound **6** with one of the seven $\mathrm{Sb}(p_z)$ bands substituted by a high-energy and a relatively flat carbon p_z band, **21**. This is so because now the central carbon connects three peripheral carbons and a high-energy antibonding carbon level should result. With the only difference that we have one instead of two electrons to place in the wide descending bands, the situation is exactly as in the closed-shell case.



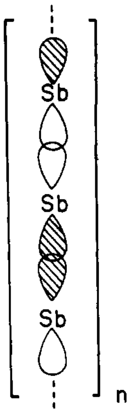
21

Other possibilities with less symmetrical types of substitution obviously exist. In such cases, the stack will tend to adopt a structure such that the carbon–carbon contacts will be reduced to a minimum with a maximum of possible antimony–antimony contacts. It is also very easy to imagine packing motifs that will create two- and three-dimensional materials that may still retain metallic band structures owing to the existence of $(\mathrm{Sb})_\infty$ chains.

Concluding Remarks

The odd alternant network of phenalenyl leads to a small HOMO–LUMO gap. Substituting carbon atoms by antimony decreases[8] this gap even further. The diminished HOMO–LUMO gap magnifies the intermolecular interactions and provides the stibaphenalenyl derivatives with a strong driving force to form infinite stacks that are sustained by strong intermolecular Sb- - -Sb bonding.

The band structures for the stacks of all the derivatives are dominated by the number (n) of Sb atoms in the stibaphenalenyl molecule. Thus, there exist n very wide bands that correspond to n $(\mathrm{Sb})_\infty$ chains, bonded via p_z atomic orbitals, **22**. These bands are crossed by n (or $n - 1$ depending on the topology of substitution) flat Sb bands, which correspond to $\mathrm{Sb}(\sigma)$ lone-pair bands, **23**, as well as by 13 − n relatively flat $\mathrm{C}(p_z)$ bands, **24**. The outcome of the avoided crossing is that in each n-stibaphenalenyl stack there exist several antimony-centered bands that are less than half-filled (or more than half-filled but less than full). Each such fractionally filled band corresponds to a band formed by stacking of closed-shell molecules that were nonintegrally charged (reduced or oxidized). In this respect, the stibaphenalenyl derivatives meet the two necessary requirements for high conduc-



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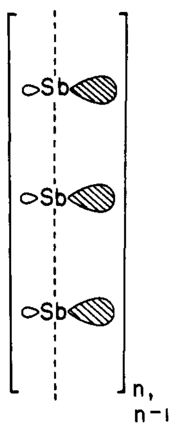

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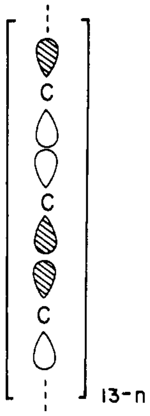

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[16] **20**, as **16** or **21**, is the schematic band structure *before* switching the interaction between the different groups of bands. This is enough for electron-counting purposes.

Table I. Exponents and Parameters Used in the Calculations

	χ_μ	ζ_μ	$H_{\mu\mu}$, eV
Sb	5s	2.323[20]	−18.8[21]
	5p	1.999	−11.7
C	2s	1.625	−21.4
	2p	1.625	−11.4
H	1s	1.3	−13.6

tivity[1] and resemble thereby the "organic metal" D–A complexes and D_2X salts.

Should the stacks of stibaphenalenyl remain one-dimensional, they would most likely be subject to CDW instabilities and undergo a metal-to-semiconductor transition at low temperatures. It is likely, however, that owing to the existence of several fractionally filled bands—some of which with a lone-pair character, **23**—the stacks will tend to interact with each other via Sb- - -Sb contacts and provide the solid with two-dimensionality, which would suppress the CDW instabilities.

There is a promise in such compounds that draws on the unique odd alternant network[2] and the presence of Sb atoms. The gradually expanding arsenal of Sb compounds and their understanding[5-8] offer some substantial benefits to the field of organometallic conductors. Thus, the incorporation of Sb (Bi) atoms into the network of conjugated organic molecules can generate compounds with low HOMO–LUMO gaps that may possess thereby (a) an inherent tendency to stack and existence of partially filled bands like the stibaphenalenyls and (b) a small tendency toward intramolecular structural localization[3c] (or small polaron binding energy[2]). In addition such molecules should be easy to both reduce and oxidize, which will lead thereby to conducting salts with two charge types.

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Appendix

The calculations are of the extended Hückel type for both molecular[17] and extended[18] systems. The modified Wolfsberg–Helmholz formula[19] was used. Exponents and parameters employed in the calculations are those of Table I. The Sb–C and C–C bond distances were taken to be 2.05[5a] and 1.40 Å, respectively.

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Two-Photon Photochemistry of $[Cu(dmp)_2]^+$

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Solutions of $[Cu(dmp)_2]^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline) in methylene chloride were observed to bleach upon exposure to high-intensity 354.7-nm pulsed-laser irradiation. The intensity dependence of the observed bleaching indicates a biphotonic process in which the second photon is absorbed by a relatively long-lived charge transfer to ligand excited state. $[Cu(dmp)_2]^{2+}$ and Cl^- appear to be formed with 1:1 stoichiometry as a result of an outer-sphere electron-transfer reaction between a high-lying excited state of the complex and a methylene chloride molecule that is presumably located in the secondary solvation shell. Bleaching, albeit less efficient, is also observed in acetonitrile, but the complex appears to be photoinert in methanol, even at very high laser intensities.

Introduction

Complexes of the type $[Cu(NN)_2]^+$, where NN denotes a heteroaromatic ligand such as 1,10-phenanthroline, are members of a class of systems that exhibit low-lying charge-transfer (CT) excited states that participate in a variety of electron-transfer processes.[1-3] In the case of the copper(I) complexes, the excitation is from (largely) metal-based orbitals to (largely) ligand-based orbitals, and the formally reduced ligand centers that result have been found to function as potent reducing agents. Net photoinduced reduction of Co(III)[4,5] and the transient reduction of Cr(III)[6] centers have been observed in solution. These systems have also been used to sensitize photocurrents at semiconductor electrodes[7,8] and, in the presence of appropriate catalysts, the formation of H_2 from H^+.[9] In addition, they have been found to undergo a novel type of exciplex quenching in the presence of Lewis bases.[10-12] For this reason most emission work has been carried out in weakly basic solvents such as CH_2Cl_2.

In an attempt to characterize the molecular and electronic structures of the $[Cu(NN)_2]^+$ systems further, we have sought to measure the time-resolved resonance Raman spectrum of photoexcited $[Cu(dmp)_2]^+$ where dmp denotes 2,9-dimethyl-1,10-phenanthroline. However, in the course of this work we have discovered that two-photon photochemistry can be induced by high-intensity laser excitation. This chemistry, which involves reductive cleavage of methylene chloride, is the subject of this report.

Experimental Section

Materials. $[Cu(dmp)_2]BF_4$, $[Cu(dmp)_2]NO_3\cdot 2.5H_2O$, and $[Cu(phen)_2]BF_4$ (phen = 1,10-phenanthroline) were prepared by a previously reported procedure.[4a] Methylene chloride and methanol were obtained from Burdick and Jackson; the acetonitrile was from Mallinckrodt. N_2O was obtained from Matheson.

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