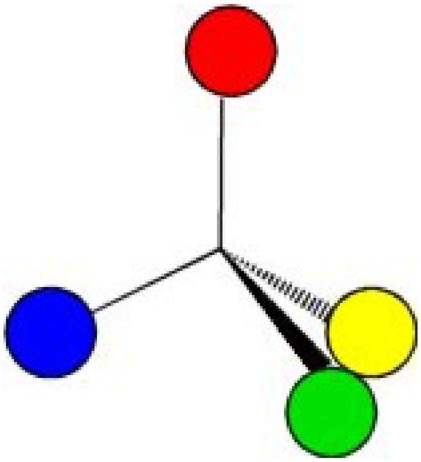

Approaching an Ambient Superconductor

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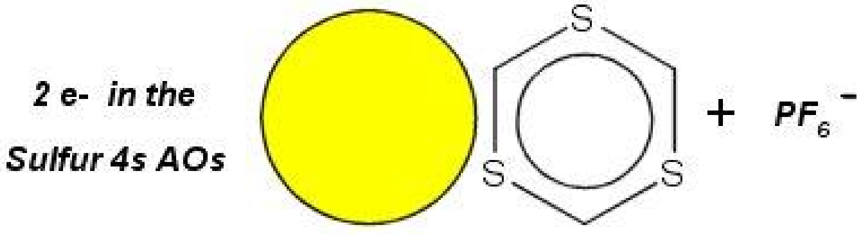
Summary

This essay discusses the structure of , and proposed synthesis routes to the compound , 1,3,5-trithiabenzenium hexafluorophosphate , $C_3H_3S_3^+$ PF_6- :



trithiabenzenium hexafluorophosphate

If it can be prepared , this sulfonium salt should be a metallic solid . It could be a **molecular metal** , with an inverse temperature – electrical conductivity relationship . It might also be a **superconductor** at very low temperatures , near absolute zero , requiring refrigeration in liquid helium . But most intriguingly , it might also be an **ambient** superconductor , that is , at 25 ºC and under one atmosphere pressure .

In conventional metallic solids , the Fermi-Dirac distribution of energies of the valence electrons in the metallic bond [conduction band] is seen as being detrimental to the formation of Cooper pairs , and therefore to the appearance of superconductivity in them , except at very low temperatures . The electronic structure of the trithiabenzenium cation is discussed , and it is shown how possible aromaticity in it may permit its highest energy metallic bond electrons to avoid a Fermi-Dirac distribution , resulting in the compound , as a crystalline solid , being an ambient superconductor .

Several synthesis routes to trithiabenzenium salts , which I believe are reasonable and practical , have been outlined .

Introduction

Ever since the phenomenon of superconductivity in metallic solids was first observed in 1911 , researchers and technologists have dreamed of discovering materials that would be fully functional superconductors under ambient conditions of temperature and pressure . Nearly a century later this goal , still formally out of reach , remains a sort of "Holy Grail" for condensed matter physicists , and in general , solid state scientists (ref. 1 , page 28) . I say "formally" , because apparently there are claims of the preparation of materials or devices exhibiting ambient superconductivity .

For example , a cursory Internet search turned up a couple of articles on the subject . On the web page , "Ronald C. Bourgoin : Ambient Temperature Bismuth Superconductor" , the inventor , Mr. Bourgoin , describes his work with micron-diameter filaments of the metalloid bismuth , culminating in a triumphal observation of zero resistance in them :

> I was down to a micron diameter of fibers. I noticed that I needed a certain voltage, and then suddenly, I got very rapid oscillations all over the place, tremendous instability, and then I would increase the current just by a little bit, and the needles would just go out of sight.
>
> The voltage went down to practically zero, as far as I could measure; the current tended to rise to infinity. Now, I didn't like the idea of having a voltage drop - they tell you, you're not supposed to have a voltage drop in a superconductor. So I worked to eliminate the voltage drop.
>
> So I learned to prepare a colloidal suspension having smaller particulates suspended, and worked at that and, my wife can tell you, I will never forget the day that this happened - I succeeded in making the suspension; I went ahead and formed the fibers as I had normally done; I took resistance measurements at the end of the trials, and they measured ZERO RESISTANCE.

(from the web page http://www.rexresearch.com/bourgoin/bourgo~1.htm)

On another web page , “Ambient Temperature Superconductivity” , by Robert Neil Boyd , mention is made of integrated circuits that functioned as ambient superconductors :

> Novellus Corporation of California was producing wafer scale integrated circuits, which were superconducting at room temperature during the late 1980's. The Novellus patent was purchased by IBM Corporation about 1989. IBM has just sat on it ever since. The basis of their fabrication technique was, again, forced production of Cooper pairing in narrow conduction channels.

(from the web page http://www.rialian.com/rnboyd/superconductivity.htm)

I have never heard of the Bourgoin or Novellus superconductors before in the print [academic] literature or even on reputable superconductor-related websites such as “Superconductors.org” (http://superconductors.org/) , so I don’t really know what to make of them . To be conservative , let us say that the universally recognized ambient superconductor has yet to be devised and synthesized . In fact , the discovery of any new high temperature superconductors seems to have gradually slowed to a halt , with the highest transition temperature for the ambient pressure superconductors holding steady at $T_c = 138$ K for a decade (since 1995) .

The very existence of an ambient superconductor was viewed for several decades as impossible by condensed matter physicists , who subscribed to the mathematical theory (later discredited by the groundbreaking research of Bednorz and Müller in 1986-87) that T_c could not exceed about 30 K . A maverick physicist , W.A. Little of Stanford University , wrote a theoretical (and somewhat heretical) paper in 1964 outlining his concept for room temperature superconductors (ref. 2 , page 28) . In Little’s scenario a polyolefin such as polyacetylene would be fitted with organic side groups in which there was some sort of electron resonance . This periodic resonance would excitonically “pump” the conduction electrons in the “spine” of the polymer . In Little’s theory , such pumping would act , at room temperature , like the phonons do at liquid helium temperature in conventional (BCS) superconductors , helping to couple them together into Cooper pairs .

Needless to say , Little’s hypothetical polymer has never been designed and synthesized in the forty years since its conception . However , his idea seems to have inspired many solid-state researchers in subsequent years . For example , the molecular and synthetic metal “stack” compounds received considerable attention and much investigation when it was realized that they might be modified to meet Little’s criteria for ambient superconductivity . Alas , such stack compounds proved to be of the “semiconductor” variety of metallic solid [a direct temperature – electrical conductivity relationship] except for a few under high pressure .

It is highly unlikely at this point in the development of new superconductors that any more high T_c compounds , let alone ambient superconductors , will be discovered serendipitously , i.e. by chance . A new approach is required to make that final climb to the summit of this very challenging peak in materials science and engineering . However , as I have pointed out elsewhere , a physical theory cannot be used to predict or design a new chemical compound . Only a chemistry-based theory or (as I like to call it) “picture” can be used to guide us in the design and synthesis of new materials , including superconductors .

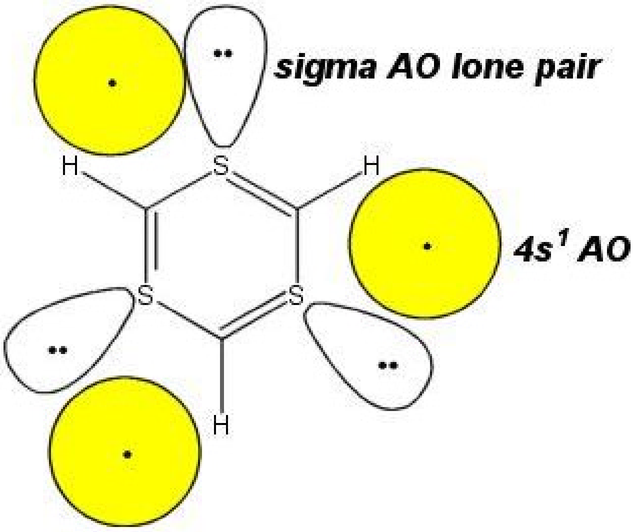
So , here is my description of a remarkable – possibly even marvelous – new chemical compound , of how it might be prepared , and my picture of how it might conceivably be an ambient superconductor .

1,3,5-Trithiabenzenium salts

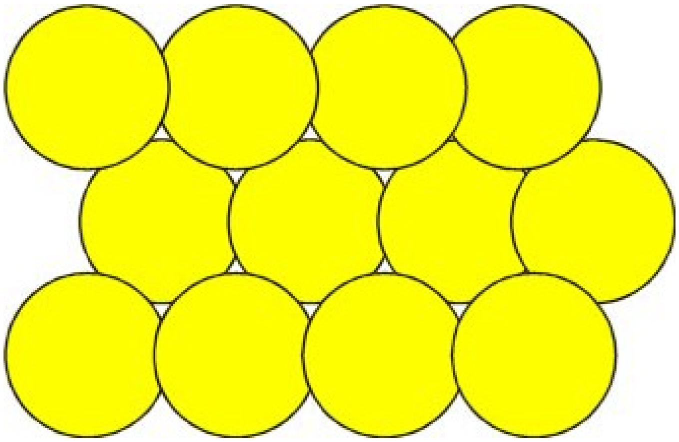
Based on a study of the macromolecular metal , poly(sulfur nitride) , $(SN)_x$, I proposed a number of new molecular metals as candidates for synthesis and study . They are surveyed in a companion report , “Designing New Molecular Metals” , freely available as a download from my website , “Chemexplore” (http://www.chemexplore.net/) . The theory underlying the design of these compounds is fully discussed in this article . In a nutshell , the technique involves the reproportionation of sulfur(II) and sulfur (IV) valence states to the “unnatural” sulfur(III) state . The sulfur atoms are all within the same molecule , and will be connected by polyolefin bonds after reproportionation . Providing the sulfur(III) species aren't part of a thiophene sort of aromatic system , the "sixth" valence electrons in the sulfur(III) atoms will be promoted energetically up into their 4s native AOs . The sigma AOs are quite voluminous , and can readily overlap within the molecule and throughout the crystalline molecular solid to form the sigma XO [crystal orbital] , which is the metallic bond , or conduction band , within the material .

Trithiabenzenium cation was designed (no , it wasn't serendipitously stumbled across !) in such a manner . My intention was to sketch out a new molecule which would contain the highest density of sulfur(III) atoms possible , so as to have the maximum overlap of their 4s AOs :

$C_3H_3S_3$: 1,3,5-Trithiabenzene Structure



In the above sketch , the sulfur(III) atoms have a trigonal sp^2 hybridization (for those readers who still appreciate the good old valence bond theory !) , similar , say , to the nitrogen atom in the pyridine molecule . Five of the six sulfur valence electrons [$3s^2$ $3p^4$] can be readily accounted for in this structure . What about the sixth electron ? I have always thought , with respect to the molecular and polymeric metals based on electronically active sulfur(III) atoms , that the sulfur 4s AOs were the logical recipient for the promoted sixth valence electrons . These sigma AOs can overlap throughout the molecular solid :



In essence , the molecular metals (based on sulfurs) are really a form of metallic sulfur , the organic skeletons being merely a sort of window dressing . The sulfur(III) atoms in these compounds are isoelectronic with the alkali metal potassium (both are $4s^1$) , although obviously the two types of materials are very different chemically . It is interesting to note , by the way , that poly(sulfur nitride) crystals are soft and malleable ; they can be rolled into sheets . When left exposed to the air , they will tarnish , their surfaces reacting with the oxygen and moisture of the atmosphere .

Most importantly , though , poly(sulfur nitride) behaves like a true metal , in that it has an **inverse** temperature – electrical conductivity relationship . Its metallic bond must therefore be similar to those in the true metals , and different from those in the semiconductors , which all have a **direct** temperature – electrical conductivity relationship . I have discussed the orbital nature of the metallic bond elsewhere at some length [in the ebook , “Exploring the Chemistry of Metallic Solids , including Superconductors” , also available free from my website] . I have suggested that in the true metals , such as $(SN)_x$ and potassium , the metallic bond is a nodeless crystal orbital above and surrounding the covalent skeleton or Inert Gas kernels , respectively , while in the semiconductors such as silicon , germanium , gallium arsenide , etc. the metallic bond is in the covalent skeletons themselves , which are nodal around the atomic kernels , a feature of the localized sigma MOs . The presence or absence of the nodes in the crystal orbitals determines their electrical conductivity and metallic character .

Returning to the sketch on page 6 , since the 4s sigma XO over each sulfur(III) atom is quite voluminous , and since the three sulfurs will be quite close together in the trithiabenzene molecule , we can reasonably expect them to overlap together in it to form a "mini-XO" over the molecule ; this is portrayed as the yellow circles in the sketches on page 2 and on page 7 (my chemistry software won't allow the yellow circle to be placed over the trithiabenzene ring , where it really should be located) . When the trithiabenzene molecules are packed together in the crystalline solid , the sulfur 4s mini-XOs can overlap throughout the lattice to form one single crystal-wide XO , which is the metallic bond , or conduction band , in it . This nodeless XO will permit the solid trithiabenzene to function as a **true metal** , as $(SN)_x$ and potassium are .

However , it might be very difficult , if not impossible , for three sulfur valence electrons to be promoted within the same molecule , because of their coulombic repulsion in the mini-XO . Even two electrons couldn't be promoted , unless they had opposite spins . That gave me the idea to remove one of the 4s electrons by one-electron oxidation . That would in effect create an intramolecular mixed-valence resonance system in the mini-XO , which should energetically stabilize it and permit the dual promotion .

It occurred to me several weeks later that there might be even more stabilization in the mini-XO than I first realized . This could occur from the aromatization of the two 4s electrons in the mini-XO . The general rule of 4n+2 valence electrons resonating in an organic molecular ring being "aromatic" , and therefore energetically very stable , might also apply to the sulfur 4s electrons . Of course , we are all familiar with aromaticity in benzene , in which n = 1 . But it is also possible to set n = 0 , which will require two valence electrons resonating in a ring system . We do indeed have those circumstances in the trithiabenzenium cation . Mind you , the 4n+2 electron rule has always been applied to the pi MO systems of carbon atoms , and we have the sigma MO – the mini-XO – of three sulfur atoms in our hypothetical compound .

So we have the interesting situation in which a lower energy level pi MO aromatic ring is formed in the molecule , with the carbon and sulfur atoms . Then above that , we have a second aromatic ring over the three sulfur atoms comprising the mini-XO . It further occurred to me that in the crystalline trithiabenzenium salt , with all the mini-XOs overlapping to create the giant XO , the aromaticity in them may be so stabilizing as to permit the aromatic pairs to migrate downfield intact , under an applied p.d. (voltage) across the crystal . I am reminded in this context of a theory proposed by Perlstein , concerning the mechanism of electrical conduction in the charge transfer compound and molecular metal , TTF-TCNQ . He suggested that the current is carried by a wave of aromaticity through the stacks of molecules in the solid (ref. 3 , page 28) .

In this picture , the aromatic pairs of sulfur 4s electrons all move simultaneously under the pull of the p.d. , from one molecule to the next . If they can do this at room temperature and pressure , then we will have ……. an ambient superconductor !

But wait a moment . What about the Fermi-Dirac distribution , which “crunches” all the valence electrons in the metallic bond , consigning 99% of them to pairing in energy levels below the Fermi level ? Won’t it also crunch the aromatic pairs into a conventional metallic bond ?

Dodging the Fermi-Dirac Distribution

Electrons in the metallic bond are normally distributed in a vast number of energy levels , paired two by two , corresponding to the number of atoms comprising the mass of the metal . In one mole [gram-atom] of elementary metal such as potassium , there would be N_A energy levels in the single metallic bond throughout the mass of metal , where N_A is Avogadro's Number (6.02257×10^{23}) . The $4s^1$ valence electrons in the potassium atoms are distributed throughout these N_A energy levels , such that about 99% of them are paired in the lower energy levels . The remaining 1% of the $4s^1$ electrons are unpaired singlets in the higher energy levels . The boundary between the paired and unpaired electrons is the Fermi level . The unpaired electrons are responsible for the physical properties of the metal , such as electrical and thermal conductivity , optical effects (reflectivity – metallic luster – and color) , and magnetic properties (Pauli paramagnetism) .

The lower paired electrons do contribute to the strength of metallic bonds , which are quite weak ; they are much weaker than covalent or ionic bonds , for example . Potassium is a very soft substance , like unhardened putty , and is quite malleable and ductile : almost "squishy" , in fact !

In my previously mentioned ebook , "Exploring the Chemistry of the Metallic Bond , etc." , I discussed a very general picture of how electrons in the metallic bond might form Cooper pairs in the superconducting state . It is easy to show , with just simple High School physics and algebra , that two electrons can actually condense together into a spin pair , providing their spins are perfectly antiparallel . This can only be accomplished in the Cooper pairs in functional superconductors . Although the similar negative electrical charges on the two electrons will indeed cause a mutual repulsion , this is overcome and far surpassed by their magnetic fields , which in the antiparallel configuration will be highly attractive , like two spherical magnets [the Earth is a spherical magnet] . It's easy to show that the ratio of the magnetic force of attraction , F_m , is almost 1200 times stronger than the electrostatic force of repulsion , F_e : $F_m / F_e = 1174$. This is a universal constant , applicable in all physical and chemical conditions . The prerequisite , as noted , is perfect antiparallelism in the two electrons . In that case , the dipoles of the spherical magnets will be aligned north-south and south-north for a maximum attraction .

In the conventional metallic bond , we can see why it must be very difficult for its electrons (above the Fermi level) to condense into Cooper pairs . The Fermi-Dirac distribution causes those approximately 1% of free unpaired electrons to be widely scattered about the geographical area of the crystal lattice . The average distance between them must be quite considerable . As a result , because of the inverse square law of the magnetic attractive force , the absolute force attracting any two pairs of free electrons must be vanishingly small , effectively nil in fact . In that event , the only possible mechanism that might conceivably form Cooper pairs in conventional metals is the BCS mechanism , which does indeed seem to function in about twenty-nine or so of the metallic elements , and many more intermetallic and other compounds .

Because phonon-mediated Cooper pairs are so thermally fragile , they can exist only at extremely low temperatures , generally considered not exceeding 30 K . From that point higher , we need another method to form them . That second mechanism was discovered in the high temperature superconductors , effectively the large family of cuprates , based on the highly antiferromagnetic copper(II) oxide .

In this second method we – in effect – do an “end-run” around the Fermi-Dirac distribution , to use a football metaphor . This is accomplished chemically , by creating in the solid a bilayer metallic bond , in which antiferromagnetic ordering is imposed on the metallic bond free electrons . The source of the antiferromagnetic ordering is the copper(II) cations , in an oxide environment , that is , coordinated by oxide anion ligands . In the bilayer metallic bond the lower energy level is contributed by the oxide anions’ $2p_z^2$ native (unhybridized) AOs , which have the correct symmetry , shape , size , and spatial orientation to overlap continuously in the lattice with the copper atoms’ $4p_z^1$ AOs [for copper (II) ; for copper (III) , $4p_z^0$] . These latter AOs form the upper , higher energy level of the bilayer pi XO . The Fermi level in this system is presumed to be at the interface between the two layers .

If this is the case , then 100% of the copper(II) free electrons will be located above the Fermi level , rather than the usual 1% or so in elementary copper metal . That means that in the high T_c superconducting cuprates such as YBCO [yttrium barium copper oxide , $YBa_2Cu_3O_7$ (idealized empirical formula)] the free electrons on neighboring copper cations will be much closer than those in copper or potassium metal . The absolute magnetic force of attraction will now be strong enough to permit the condensation of the free electrons into Cooper pairs at a much higher temperature than with those formed by the BCS mechanism . With the bilayer metallic bond mechanism we can now prepare superconductors with transition temperatures ranging from about 30 K up to the existing record high of 138 K .

Note that the antiparallelism requirement for the spin pairs is provided by the antiferromagnetic régime imposed on the free electrons in the pi XO metallic bond by the oxide coordinated copper(II) cations . In fact , high T_c superconductivity has been observed only in materials whose parent non-metallic base compound exhibited a strong antiferromagnetism . Then , the nonmetallic base compound was doped to produce a Robin-Day Class II mixed-valent compound , in which the metallic bond (pi XO) was activated . The antiferromagnetism was imposed on the copper(II) free electrons [$4p_z^1$] , resulting in their antiparallelism . Then the magnetic polar coupling force , as feeble in absolute terms as it undoubtedly was , acted on the neighboring free electrons to condense them into Cooper pairs .

Even this second mechanism of producing Cooper pairs obviously has its temperature limitations . To reach ever-higher transition temperatures for superconductivity we must devise a third mechanism for binding the spin pair electrons even more strongly . This third mechanism must , like the second one of the bilayer metallic bond , also “do an end run” around the Fermi-Dirac distribution .

Given that the pi MO of the carbon-sulfur aromatic ring of the trithiabenzenium cation is also a delocalized electron system , and that it is comprised of carbon and sulfur derived valence electrons , it might be able to act as the lower energy layer of a hypothetical carbon-sulfur metallic bond in the solid . Then , the sulfur-only sigma XO could form the upper layer of the crystal-wide XO . The sulfur aromatic pairs could thus avoid the Fermi-Dirac distribution , which would otherwise disperse them in the vast multiplex metallic bond . Failing that , the trithiabenzenium salt would probably have a transition temperature in the 10-20 K range (my guess) , making it a more or less conventional molecular metal .

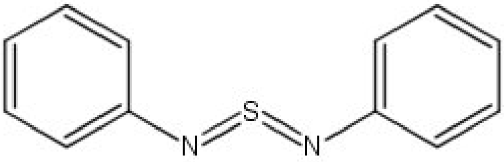
That brings us to another uncomfortable point . Because of their cationic charges , the trithiabenzenium cations wouldn't be able to form nicely aligned stacks of molecules , as in the "poker chip" analogy often used to describe the "self" stacks of the molecular metals such as TTF-TCNQ . In this latter compound , the stacks are "self" because of the metallic bond that forms down the spine of the sulfur-containing component , TTF . In order to form that metallic bond , sufficient numbers of neutral TTF molecules must be inserted in between the TTF cations in order to dilute their repulsive electrostatic charges . The self stacks form when a balance between the various competing molecular bonding forces (metallic bond , ionic repulsions , van der Waals bonds) has been achieved . However , the parent neutral trithiabenzene molecule will be unavailable in our case ; it is likely too unstable to be prepared . Thus the trithiabenzenium molecules probably won't be in any sort of stack arrangement in the crystalline solid . All we can hope for , then , is that the sulfur 4s sigma "mini-XOs" will be sufficiently voluminous to overlap from molecule to molecule to form a strong enough crystal-wide XO to serve as the metallic bond .

Synthesis routes to the trithiabenzenium cation

It's fun to speculate and theorize about a certain material , but can it actually be made ? In this case , I think so , and in a reasonably efficient manner , although some "pure" chemistry research might be needed first .

This is because of the necessity of reproportionating the sulfur(II) and sulfur(IV) valence states to the metallic sulfur(III) state . Sulfur(II) organic compounds are well known , as in the sulfides (thioethers) . Inorganic sulfur(IV) compounds are fairly common : for example , the industrial pollutant gas sulfur dioxide ; the organic synthesis reagent thionyl chloride ; and the powerful fluorinating agent , sulfur tetrafluoride . However , sulfur(IV) organic compounds are rather rare creatures . We have to reproportionate sulfide , $R_1–S–R_2$, with sulfurane , $R_1=S=R_2$, to obtain $R_1–S=R_2(e-)$.

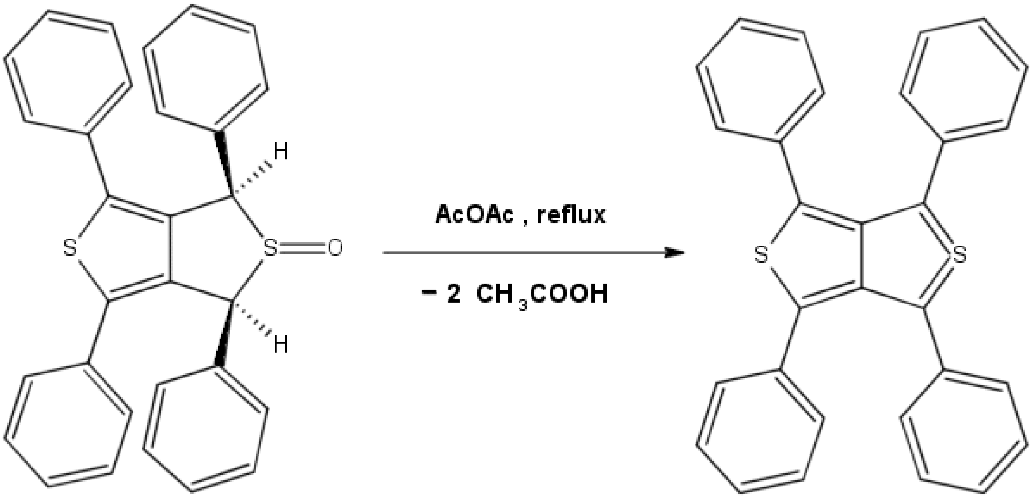
It's easy getting the sulfide part , but the sulfurane functionality is little known . The compound bis(phenylimino)sulfurane has been prepared from the condensation of two equivalents of aniline with one equivalent of sulfur tetrafluoride (ref. 4 , page 29) :



bis(phenylimino) sulfurane

b.p. 114 C (0.8 mm) , "bromine-colored"

Carbon sulfuranes appear to be as yet unknown . The dehydration of a sulfoxide to a sulfurane-like species has been described by Cava and Husbands (ref. 5 , page 29) :

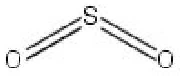


tetraphenylthieno[3,4-C] thiophene , 87% yield

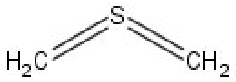
"glistening purple needles" , m.p. 245-248 C

Note that both thiophene rings in the product are aromatic , so that the right-hand ring really isn't a sulfurane . Also , the dehydration reaction was undoubtedly facilitated by the aromatic stabilization in the product . It might not succeed in the preparation of non-aromatic sulfuranes .

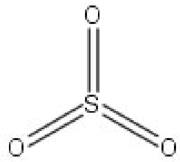
I see no theoretical impediment to the existence of carbon sulfuranes , which should be isoelectronic and isostructural with sulfur dioxide :



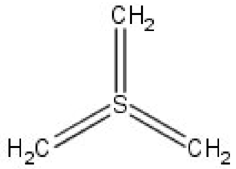
sulfur dioxide



bis(methylene)sulfurane



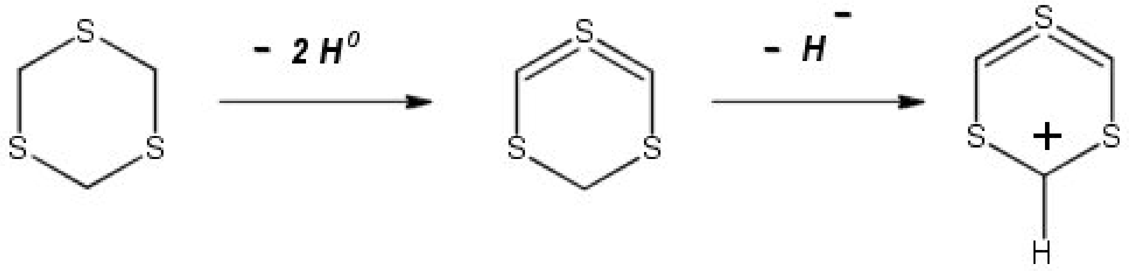
sulfur trioxide



tris(methylene)sulfurane

A cursory check in Chemical Abstracts failed to reveal any mention of the hypothetical compound C_2H_4S , as bis(methylene)sulfurane . However , searches in Chemical Abstracts tend to be rather mind-numbing affairs , and I might have missed a mention of it , particularly in the last decade , whose volumes were missing at my library . Interested researchers should , of course , conduct their own literature search , preferably of electronic databases , if available – a lot easier than in the printed volumes !

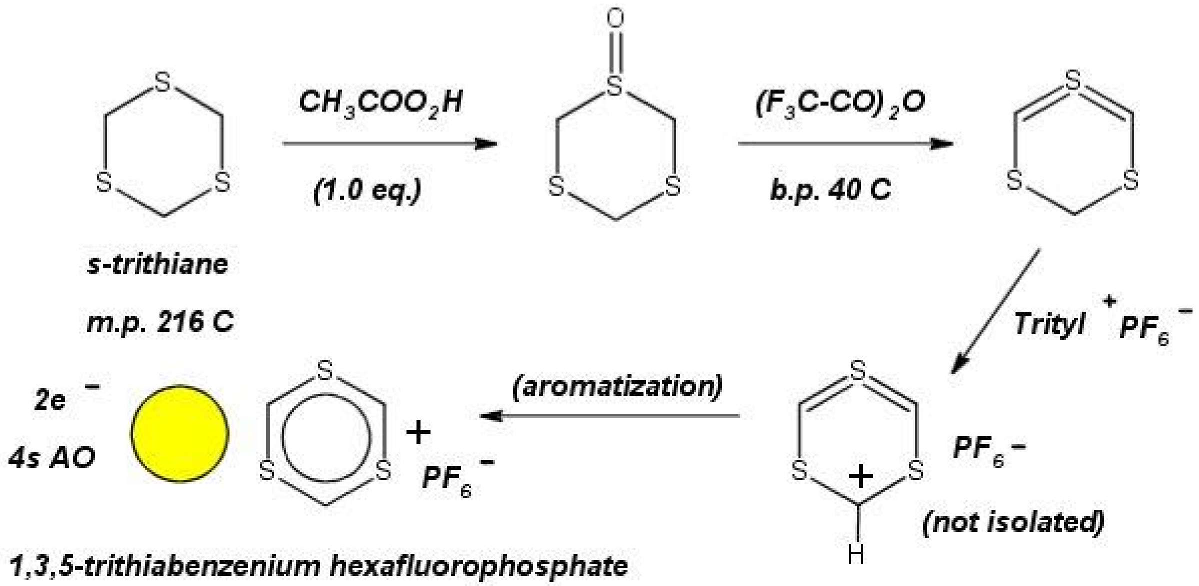
Our target molecule would be 1,3,5-trithiacyclohexa-1,6-diene :



s-trithiane **1,3,5-trithiacyclohexa-1,6-diene**

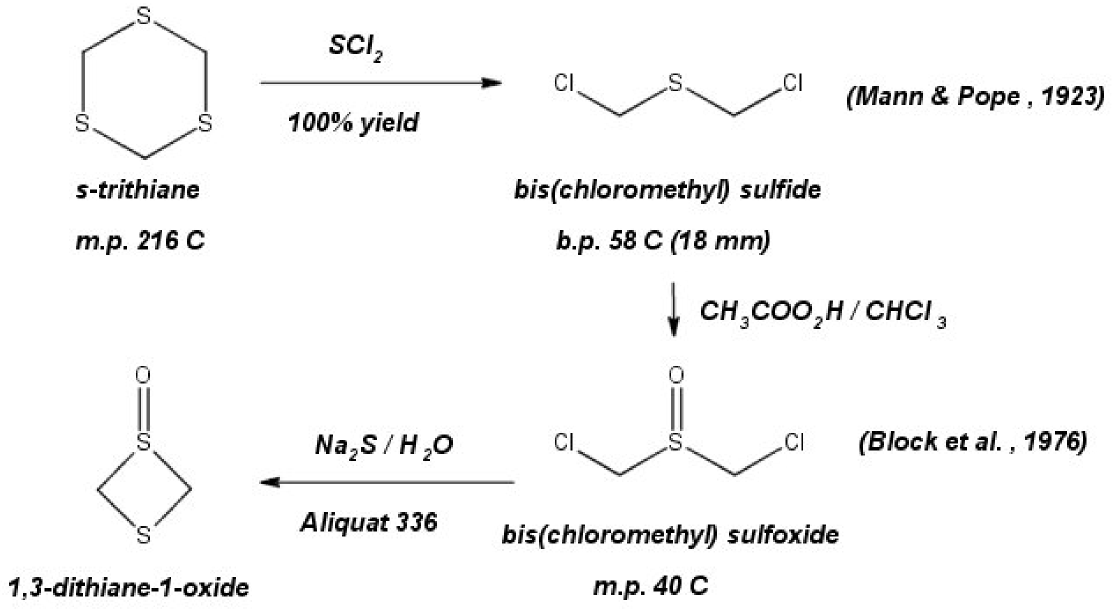
This latter molecule should be easy to convert to the corresponding cationic form by the chemical technique of hydride abstraction . The cationic form shown above should – theoretically – instantly aromatize into the trithiabenzenium cation , because of the considerable energy stabilization of its two aromatic rings (the lower energy pi , and the higher energy sigma) .

The logical starting material for the synthesis of the trithiabenenzenium cation would be s-trithiane [a contraction of 1,3,5-trithiacyclohexane , where “s” stands for “symmetrical”] . This is a well-known , commercially available organic reagent , eg. from the Aldrich Chemical Company . It is insoluble in water , and melts at about 216 ºC (another reference says 220 ºC , crystallized from acetic acid) . A possible route to the trithiabenzenium cation is shown in the following scheme :



In the first step , trithiane would be oxidized on one of the sulfurs by peracetic acid , CH_3–CO–OO–H . This reagent is commonly prepared in situ , as required , by dissolving the appropriate quantity of 35% H_2O_2 in acetic anhydride (ref. 6 , page 29) . Apparently trithiane is soluble in glacial acetic acid , so this would probably be a suitable solvent for both the substrate sulfide and the oxidizer , the peracetic acid . Control of the reagent quantities and reaction conditions should permit the preparation of the monosubstituted sulfoxide , 1,3,5-trithiane-1-oxide .

An alternate route to the sulfoxide was suggested by the research of Block et al. in 1976 (ref. 7 , page 29) , who prepared the compound 1,3-dithiane-1-oxide :

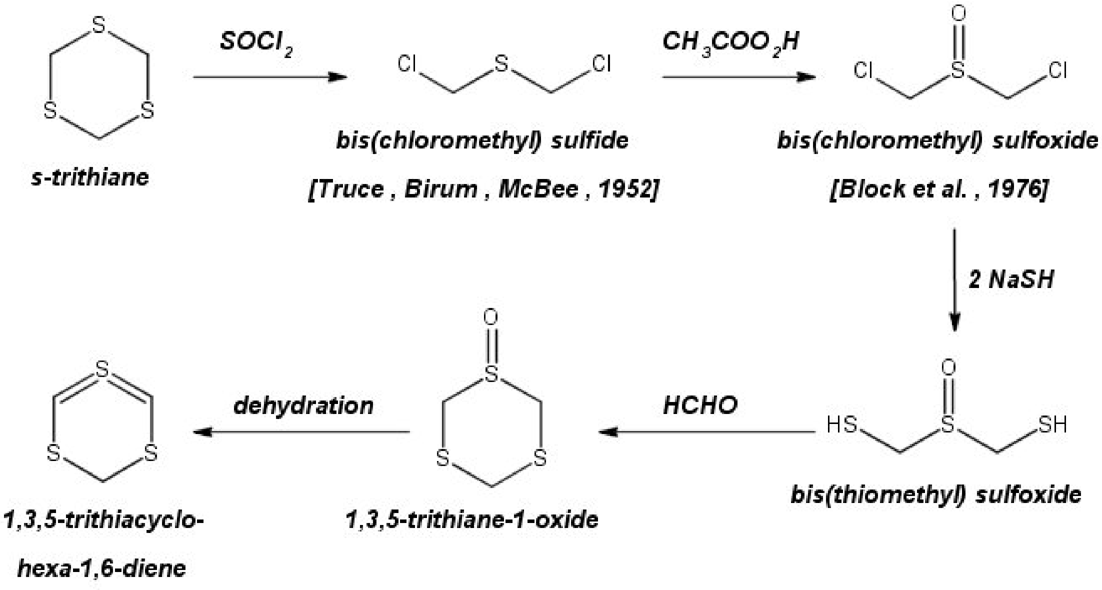


By substituting the inorganic reagent sodium sulfhydride , NaSH [the hydrated form is commercially available and is inexpensive] , for the sodium sulfide , we should be able to prepare bis(thiomethyl) sulfoxide , which could be cyclized with formaldehyde to provide trithiane-1-oxide , as shown in the scheme at the top of the next page .

In the second step , a dehydrating agent would be used to convert the sulfoxide into the sulfurane . Based on the work of Cava and Husbands illustrated above on page 14 , I have suggested the reagent trifluoroacetic anhydride , $(F_3C\text{–}CO\text{–})_2O$, which is more volatile than the corresponding acetic anhydride used by those researchers :

acetic anhydride : b.p. 138-140 ºC
trifluoroacetic anhydride : 40 ºC

acetic acid : 116-118 ºC
trifluoroacetic acid : 72 ºC



Note : an efficient preparation of bis(chloromethyl) sulfide was described by Truce , Birum , and McBee in 1952 (ref. 8 , page 29) .

The removal of unreacted excess trifluoroacetic anhydride , along with the by-product trifluoroacetic acid , could be readily accomplished by a simple technique such as rotary evaporation in vacuo , after testing , eg. by TLC , had confirmed a complete conversion of the sulfoxide to the sulfurane . Note that the latter compound might be subject to a facile rehydration to the sulfoxide , so it would have to be kept tightly sealed in a desiccator , away from atmospheric humidity .

A half-dozen or so other reagents are known to be effective at dehydrating alcohols ; they might also succeed in dehydrating the sulfoxide to the sulfurane . Concise reviews of these chemical systems are provided by Fieser and Fieser (ref. 6 , page 29) :

Dicyclohexylcarboimide , hydrated to dicyclohexylurea ;
Phenyl isocyanate , hydrated to aniline and CO_2 ;
Vilsmeier’s reagent (dimethyl formamide + $SOCl_2$) ;

Pyridine + $SOCl_2$;
Pyridine + $POCl_3$; and ,
p-Toluenesulfonic acid in toluene , with azeotropic distillation of water into a Dean-Stark tube .

All of these reagents are strong electrophiles which bond strongly to the electronegative oxygen atom of the sulfoxide group ; for example ,

$$S{=}O + (F_3C{-}CO{-})_2O \longrightarrow S({-}O{-}CO{-}CF_3)_2 \text{ ; then ,}$$

$$S({-}O{-}CO{-}CF_3)_2 \longrightarrow {=}S{=} + 2\ F_3C{-}CO{-}COOH \text{ .}$$

$$S{=}O + 2\ TsOH \longrightarrow S({-}O{-}Ts)_2 + H_2O \text{ ; then ,}$$

$$S({-}O{-}Ts)_2 \longrightarrow {=}S{=} + 2\ TsOH$$

, where TsOH is p-toluenesulfonic acid .

That's where the "pure" chemistry comes in , as these sorts of reactions are of course unknown ; indeed , the chemistry of the sulfurane group , =S= , is essentially unexplored as well .

Assuming that the target molecule , 1,3,5-trithiacyclohexa-1,6-diene (page 15) can be successfully synthesized and characterized , the final step would be hydride abstraction from it to produce the corresponding cationic intermediate (with the carbocation formally on C4) . I expect this would be a very transient species , aromatizing spontaneously to the trithiabenzenium sulfonium salt . Several reagents are known to be efficient hydride abstractors , provided there is an energy stabilization in the products relative to the substrates .

The first of these is the trityl carbocation [triphenylcarbenium salts] , Ph_3C^+ X- , where "X" is an inert spectator anion , such as ClO_4- , BF_4- , PF_6- , AsF_6- , and SbF_6- . One method of preparing them is by combining trityl alcohol [triphenylcarbinol] with the corresponding mineral acid :

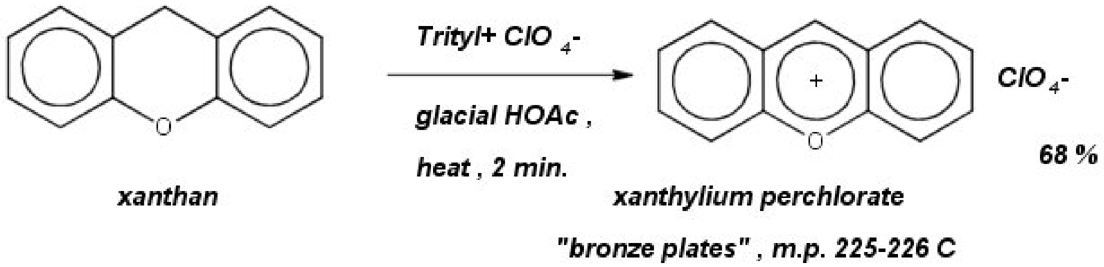
$$Ph_3C{-}OH + HBF_4 \longrightarrow Ph_3C^+\ BF_4^- + H_2O \text{ .}$$

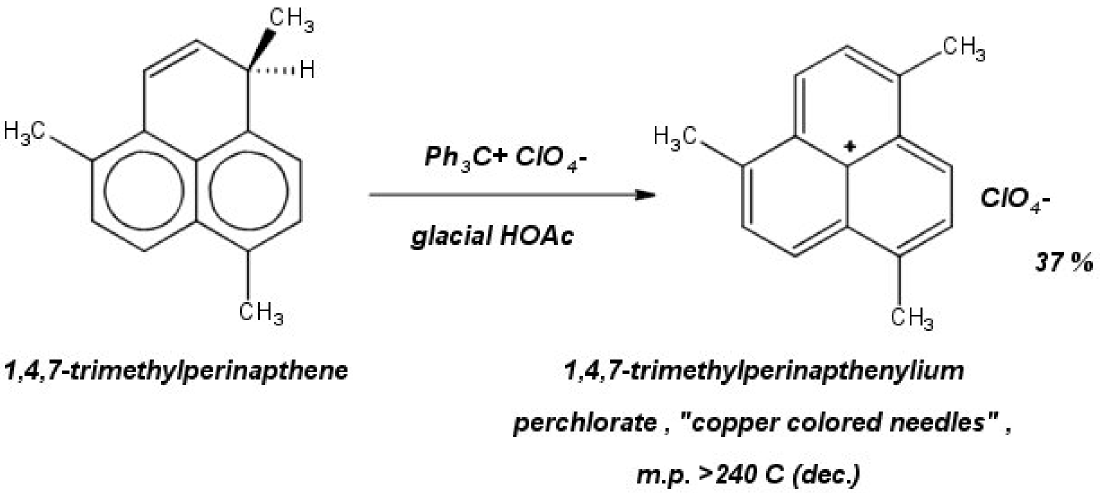
(ref. 9 , page 29) .

The trityl salts are also commercially available , but are rather expensive .

The trityl carbocation will extract hydrogen atoms , formally as hydride , from suitable substrates , generally those yielding either aromatic products or at least with highly conjugated systems , as shown in the following two examples :

Bonthrone & Reid (1959) :

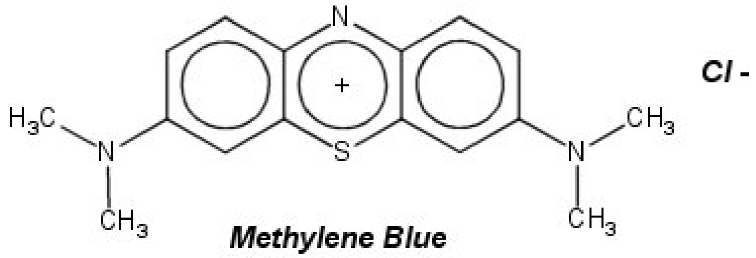




(ref. 10 , page 29) .

I didn’t show it in the sketches above , but the trityl cation is reduced to triphenylmethane , Ph_3CH , m.p. 92-94 ºC , which will be a by-product in these hydride abstraction reactions .

The xanthylium perchlorate oxonium salt is reminiscent of the aromatic sulfonium salt methylene blue , which is a well-known , deep blue dye :



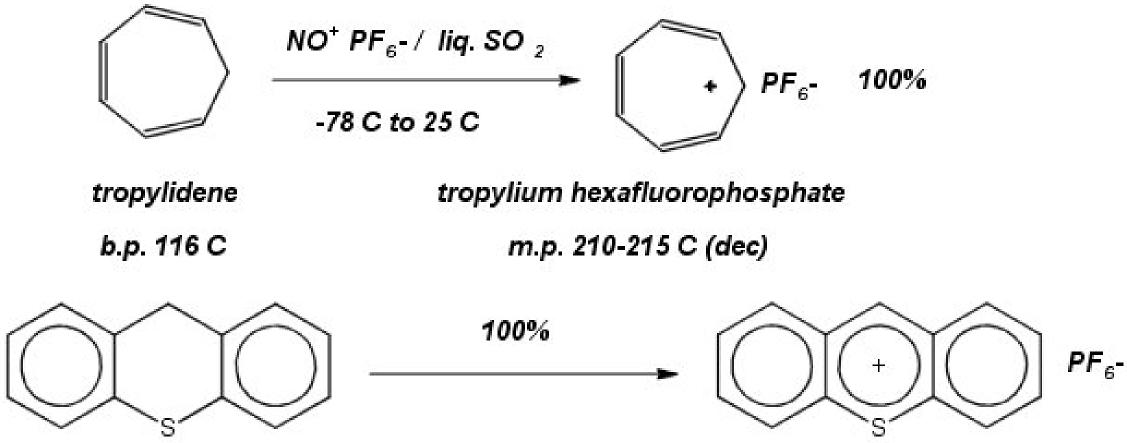
A second hydride abstraction reagent is the nitrosonium cation , NO^+ , which is actually a moderately strong oxidizer :

$$NO^+ + e- \longrightarrow NO\ (g) \quad ; \quad E^0_{red} = 1.45\ V\ .$$

Olah and coworkers have studied a half dozen hydride abstraction reactions using nitrosonium hexafluorophosphate as the oxidizer (ref. 11 , page 29) . Two interesting examples of their research in this area are sketched on the next page .

Both $NO^+ PF_6$- and $NO^+ BF_4$- are commercially available , eg. from Alfa Aesar , as crystalline salts . Olah's team preferred the hexafluorophosphate reagent because of its higher solubility in reaction solvents than the tetrafluoroborate compound . A polar organic solvent such as acetonitrile can also be used in place of the liquid sulfur dioxide (b.p. -10 ºC) cited in the two reactions outlined below . The hydride abstractions all proceeded in high , and often quantitative , yields under mild conditions . Because of its relatively strong oxidizing power , the nitrosonium cation seems to be a more powerful hydride abstraction reagent than the trityl carbocation , and would be my first choice in the proposed reaction with the sulfurane substrate 1,3,5-trithiacyclohexa-1,6-diene .

Olah et al. (1978) :



tropylidene

b.p. 116 C

tropylium hexafluorophosphate

m.p. 210-215 C (dec)

thioxanthene

m.p. 128 C

thioxanthenylium

hexafluorophosphate

The third hydride extraction reagent is another inorganic compound , antimony pentachloride . The same sorts of reactions shown immediately above can also be carried out with $SbCl_5$. For example , Holmes and Pettit have described their experiments using antimony pentachloride to form a variety of resonance-stabilized carbocation salts (ref. 12 , page 30) . The general reaction is :

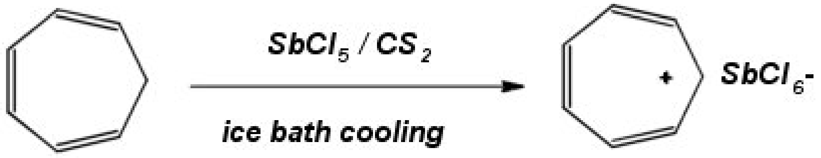
$$R\text{–}H \ + \ 2\ SbCl_5 \longrightarrow R^+ \, SbCl_6- \ + \ SbCl_3 \ + \ HCl\ (g) \ .$$

Two of their reactions of antimony pentachloride with organic substrates are sketched on the next page . The yields were excellent in all cases .

Having said that , however , we suspect that the $SbCl_6$- anion would likely be unsuitable in any molecular metal synthesis . Sb(V) is well known to be mildly oxidizing :

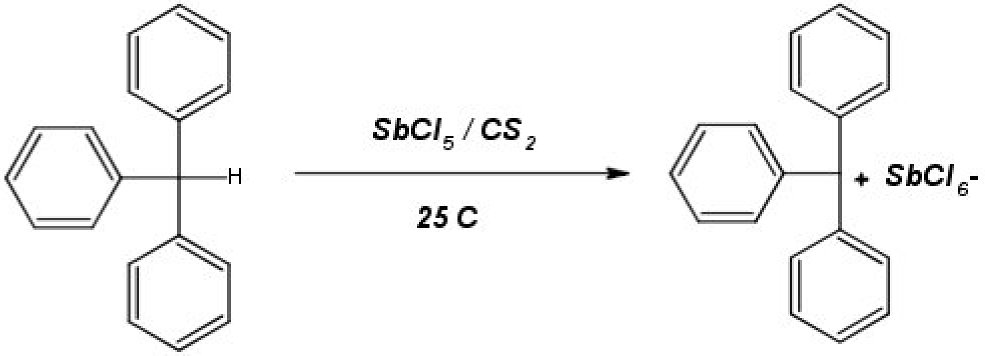
$$Sb(V) \ + \ 2\ e- \longrightarrow Sb(III) \ ; \ E^0_{red} = 0.82\ V \ \text{(chloride environment)} \ .$$

Holmes and Pettit (1963) :



tropylidene **tropylium hexachloroantimonate**

b.p. 116 C **"pale yellow prisms" , m.p. 190 C**

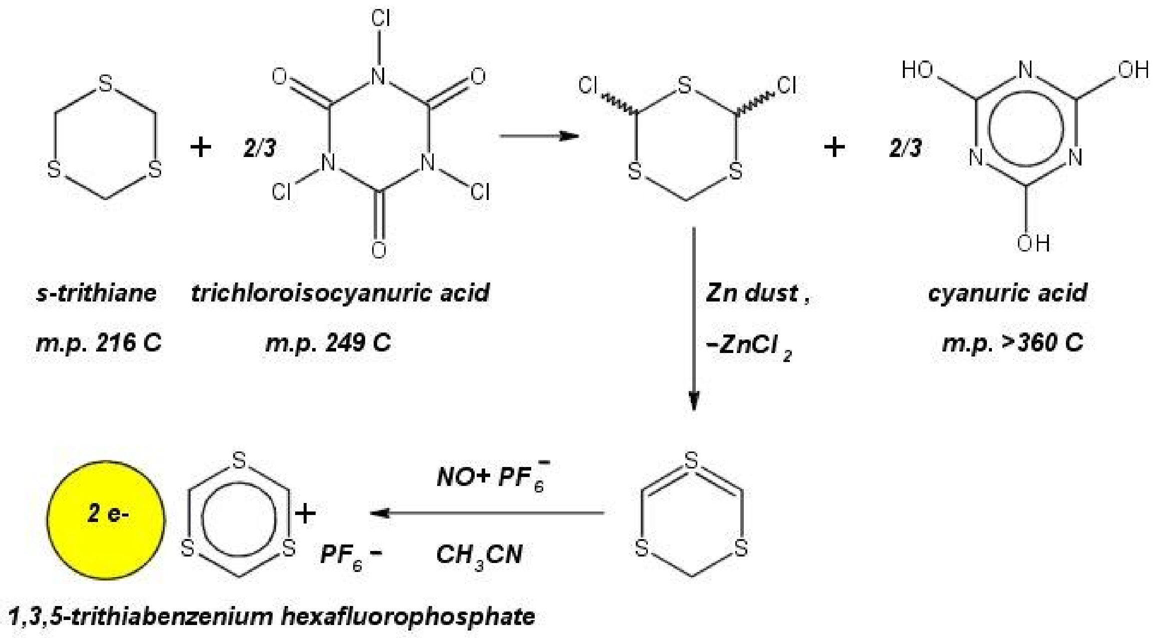


triphenylmethane **triphenylmethyl hexachloroantimonate**

m.p. 92-94 C **"yellow prisms" , m.p. 218 C**

That is , the $SbCl_6$- anions themselves would be oxidizing , and that could spell trouble for the free electrons in the metallic bond that stray too near them . A charge density wave would form in the lattice , with regions of free electron concentration centered around the antimonate anions . The $SbCl_6$- salt would likely be a poor semiconductor at best . Phosphorus(V) is redox-inert , so PF_6- is innocuous in the lattice , as we know from the various molecular metals in which it is found as a spectator anion .

To complete the discussion of possible synthesis methods for the trithiabenzenium cation , the following scheme (sketched on the next page) might provide another route to it .



Trichloroisocyanuric acid is a powerful chlorinating agent , available on both the laboratory scale as a pure reagent chemical , and industrially as a swimming pool disinfectant . As a crystalline solid , it is easy to weigh , handle , and use in chlorinations . The reaction of “trichlor” with excess tetrahydrofuran and tetrahydropyran in both cases provided the corresponding 2,3-dichloro-ethers in a mediocre (26-28%) yield . The reactions were quite exothermic , and required cooling and excess ether for moderation . The chlorinated products were somewhat unstable , and tended to decompose at and above room temperature (ref. 13 , page 30) . Based on this experience I have suggested that it might be possible to use “trichlor” to dichlorinate s-trithiane at C2 and C6 . An inert halogenated solvent such as dichloromethane (b.p. 40 ºC) or chloroform (b.p. 61 ºC) might be helpful in this reaction .

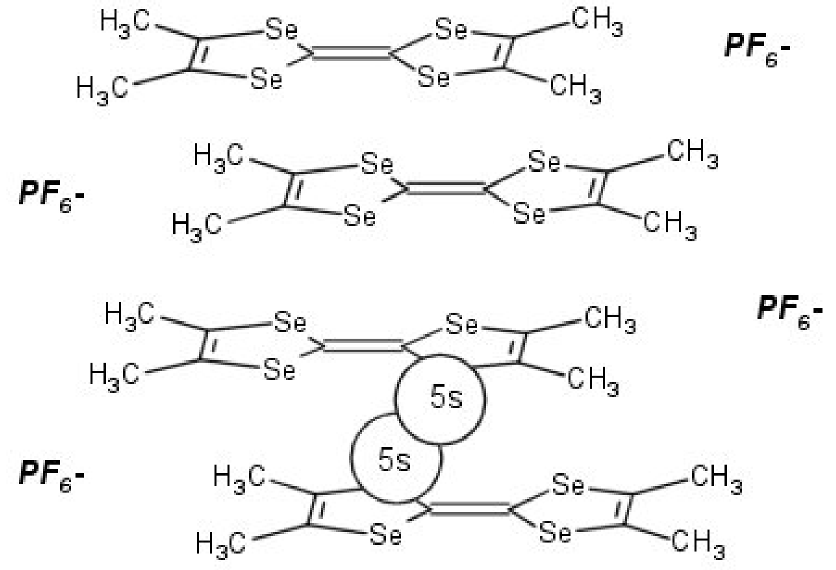
Zinc dust has been used in organic syntheses as a dehalogenating agent (see in Fieser and Fieser’s book cited in ref. 6 , page 29) , and it could be tried here as well . Removal of the two chlorine atoms should result in the formation of the desired sulfurane intermediate . I would be concerned about complexation of the by-product zinc cation with the sulfurane , as sulfur has a strong affinity for transition metals in almost any form . Possibly the zinc cation could be preferentially chelated , eg. by EDTA , to release the sulfurane and permit its extraction by a suitable solvent .

Additional thoughts

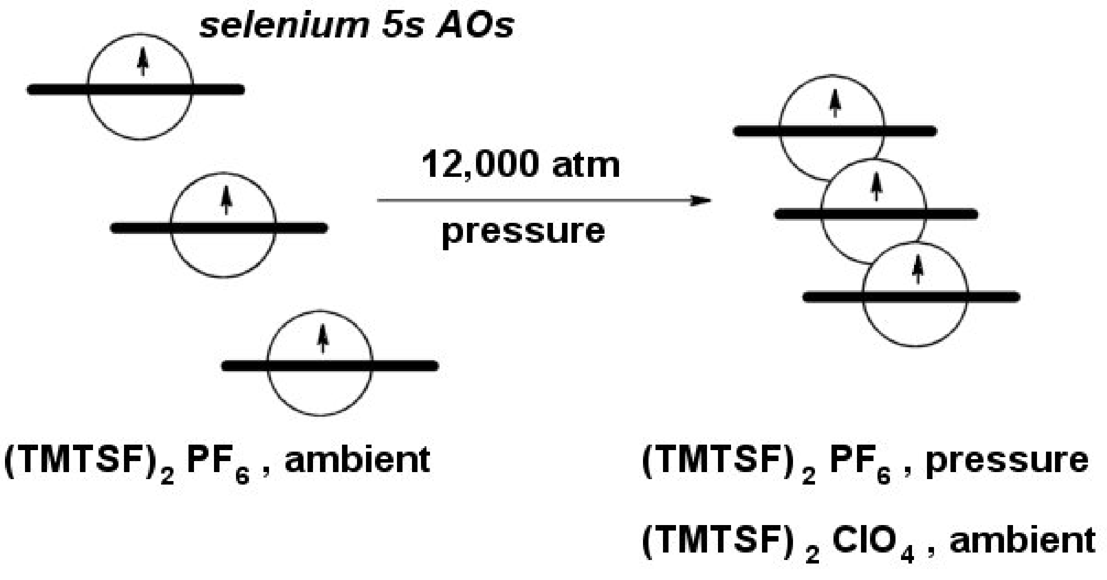
Although I have suggested the use of the hexafluorophosphate anion with the trithiabenzenium cation , it may or may not be the best one for optimizing electrical conductivity in the compound . In the molecular metal $(TMTSF)_2^+$ X- , the perchlorate anion , ClO_4- , proved superior in this respect to PF_6- . The hexafluorophosphate compound was actually a pseudometal [semiconductor , with a direct temperature – electrical conductivity relationship] , while $(TMTSF)_2^+$ ClO_4- was a true metal , with an inverse relationship , and was a superconductor with its $T_c = 1.2$ K . However , when $(TMTSF)_2^+$ PF_6- is compressed at 12 kbar , it became a true metal and a superconductor with its $T_c = 1.0$ K (ref. 14 , page 30) .

It may well be that the 4s sigma AO in the sulfurs and the 5s AO in the seleniums of TMTSF molecular metals are “muted” or “pygmy” orbitals , with only a short range of overlap . The 4s AO in sulfur , a nonmetal element , may be partially diverted into hybridization with p AOs , thus reducing its volume . By comparison , the valence s AOs of the metallic elements are less hybridized , and so are larger by comparison .

In the TMTSF compounds , use of the smaller perchlorate spectator anion may have tipped the scales in favor of a successful 5s AO overlapping in the crystal lattice , to form the metallic bond . The larger PF_6- anion , on the other hand , pushed the TMTSF molecules apart just enough to create gaps between the 5s AOs . These gaps in effect acted as “nodes” in the crystal-wide XO serving as the solid’s metallic bond . The presence of nodes of any sort in a XO makes the material behave as a pseudometal [semiconductor] . Strong compression allowed the 5s AOs to overlap enough to close the gaps and eliminate the nodes in the XO . The little sketch on the next page illustrates this simple orbital picture in the two TMTSF compounds .



(TMTSF) $_2^+$ PF$_6$- Molecular Metal Stack Compound



The choice of an appropriate spectator anion for the trithiabenzenium cation may well be critical for determining its electrical conductivity behavior , including any superconductor properties . If PF_6- is used as the anion , the researcher may be faced with the unappetizing prospect of having to compress the material to thousands of atmospheres to make it electrically conducting , let alone superconducting . The trithiabenzenium compounds , for example , could be only semiconductors at STP , but could be true metals and superconducting under high pressure , possibly even at ambient temperature !

That brings us back to the point raised earlier on page 13 , concerning the crystal structure of the trithiabenzenium compounds . Since their molecules are entirely cationic in nature , and homovalent , they are unlikely to crystallize in stacks like the conventional molecular metals . Stacking has the dual advantages of permitting an exceptionally close packing of the molecules , which in turn facilitates the formation of a strong metallic bond down the spines of the stacks . These advantages would be absent in a homovalent cationic system , which could prevent the successful overlap of the sulfur 4s AOs and the creation of the metallic bond in the solid .

If the trithiabenzenium compounds turned out to be “ordinary” , that is , non-metallic in nature, they could be converted into mixed-valent compounds of the Robin-Day Class IIIB variety [in my classification of metallic solids , Class 4] by the technique of electrocrystallization . In this process , zerovalent trithiabenzene molecules are inserted in between the cationic molecules , diminishing the repulsive cationic electrostatic charges to such an extent that the molecules can pack together and a metallic bond can form along the stacks .

Chemically , the trithiabenzenium salt would be dissolved in an inert , polar organic solvent (propylene carbonate , PC , is recommended for this application ; see ref. 15 , page 30) , together with an electrolyte , such as a lithium salt , and placed in the cathode chamber of an electrolysis cell . The lithium salt solution in PC is placed in the anode chamber to complete the circuit . I would also suggest dissolving the appropriate quantity of a “sacrificial” reducing agent , such as tetrakis(dimethylamino)ethylene [TDAE] , with a standard oxidation potential comparable to that of zinc metal , in the anolyte . The trithiabenzenium cations would be drawn to the cathode , where some of them would be reduced to the transient zerovalent trithiabenzene molecules . Crystals of the mixed-valent [zerovalent and cationic] trithiabenzenium compound would hopefully grow on the cathode surface , and also hopefully would have a elongated acicular (needle-like) shape , which is highly desired for electrical testing . A surface-active agent – surfactant – could be added to the catholyte to encourage this acicular crystal habit in the whiskers' growth (ref. 16 , page 30) .

Because of the presence of unpaired free electrons in the metallic bond of this stack compound , we would expect it to behave like a conventional molecular metal . It might then become superconducting only at extremely low temperatures , perhaps in the 10-20 K range .

Whatever the final outcome of experimentation with the trithiabenzenium cation might be , it would certainly be very instructive to synthesize and study . A new type of organic functionality , the sulfuranes , would have to be explored and developed , and the potential for synthesizing a novel two electron aromatic ring is also alluring . And of course , there is the ultimate pot of gold at the end of the rainbow for the intrepid materials scientist : an ambient superconductor . This goal may remain forever elusive , but in its pursuit many new pages in the Book of Chemistry will have been written .

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