

Theoretical Tinkering: The Search for Magnetically Ordered Organic Polymers Built From Sulfur, Carbon, Nitrogen-Containing Five-Membered Rings

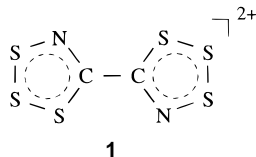
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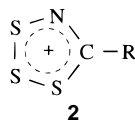
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ABSTRACT: The intriguing bis(1,2,3,4-trithiazolium) dication $(\text{CNS}_3)_2^{2+}$ is a triplet state system, even in the solid state. Prompted by this molecule, we propose and theoretically study several hypothetical polymers, in the hope that they will display magnetic ordering. We seek systems in which the valence band is half-filled and as narrow as possible. In order to achieve that, we use as monomer units the members of a fascinating family of seven- π -electron, five-membered heterocycles which are closely related to $(\text{CNS}_3)_2^{2+}$. In these compounds, the highest two π orbitals are "distinct" from all the other orbitals. The uniqueness of these orbitals carries over in a systematic way into the extended systems (*ortho*- or *meta*-linked) which they form. Because the monomers have seven π electrons, the polymers have half-filled valence bands. We try to exploit the differences among the many possible heterocycles to provide polymers with narrow valence bands. Three such polymers, poly(*cyclo*-CSSSC⁺), poly(*cyclo*-CSSNC), and poly(*cyclo*-CSNSN⁺), are found to have valence bands approximately 0.3 eV wide; the first two are helical, and the third is planar.

In 1993, the Passmore group synthesized the hexafluoroarsenate salt of an intriguing dication, bis(1,2,3,4-trithiazolium), **1**.¹ This compound forms a brown solid at room temperature, and dissolves in SO₂ to form a green liquid,² both of which display paramagnetic behavior consistent with two unpaired electrons per formula unit. X-ray analysis revealed the dication to be planar and centrosymmetric.



The dication consists of two *cyclo*-CNSSS⁺ rings, connected through their carbon atoms at a typical C(sp²)-C(sp²) singly-bonded distance of 1.46 Å. Consider one such ring, as in **2**. This ring is also known



experimentally, with CF₃ as the R group.³ Each sulfur atom contributes two electrons to the π system, while carbon and nitrogen each contribute one, so that, taking into account the +1 charge, **2** is a seven- π -electron radical. (Throughout this paper we have used a dashed ring symbol to indicate the expected delocalization of the π electrons in these systems. This symbolism carries no implication of that delocalization being stabilizing or not.)

In fact, a whole family of similar compounds is known from the work of the Passmore group and others,⁴ consisting of seven- π -electron, five-membered heterocyclic rings, among which are *cyclo*-(CR)SNS(CR),⁵ *cyclo*-(CR)NSSN,⁶ *cyclo*-(CR)SNSN,⁶ and *cyclo*-(CR)SSS(CR)⁷

(R = various ligands), as well as several analogous selenium compounds.⁸ These radicals are known to display paramagnetic behavior too, consistent with one unpaired electron per ring; Hartree-Fock calculations confirm that the unpaired electron resides in the π system.^{1,2,7}

The existence of seven- π -electron radical heterocycles is not unusual, as attested by the existence of all the above-mentioned compounds. What is quite unusual, though, is the presence of paramagnetism in any of these purely organic systems in the liquid, and rarer still in the solid state. All of these heterocycles form paramagnetic liquids; only *cyclo*-(CR)SSS(CR) and **2** retain their paramagnetism when in solid form. Even more unusual are non-metal containing moieties with *two* unpaired electrons in the solid state, which do not owe their paramagnetism to steric hindrance. Only solid O₂ and the dication **1** qualify as such.¹

Because of their unique properties, some of these heterocycles have been the focus of recent attempts to synthesize molecular organic conductors as well as organic magnets and light-emitting diodes.⁹ Our interest in these systems arises from yet another possible application: high-spin polymers.

Magnetic polymers made of purely organic components are a holy grail of modern polymer research.¹⁰ They could, ideally, combine the structural versatility of organic polymers with the desirable physical property of ferromagnetism; their organic nature would allow for highly detailed tailoring of both structural and magnetic features. None have as yet been synthesized.¹¹

The synthesis and properties of **1** suggested to us a theoretical approach for finding high-spin organic polymers, which we describe below. How will we know if the hypothetical polymers we propose are indeed high-spin or magnetic? Our criterion is simple (some would call it simplistic) and qualitative: we merely seek polymers with a narrow, half-filled valence band, because such a feature in the electronic structure is often

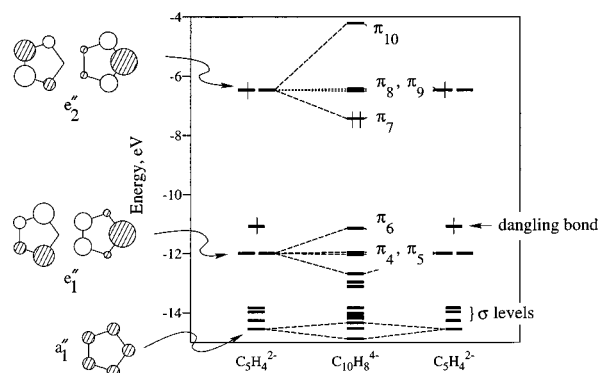


Figure 1. Orbital interaction diagram for two Cp-like $C_5H_4^{2-}$ groups combining to form a fulvalene-like $C_{10}H_8^{4-}$ molecule. The π orbitals of the $C_5H_4^{2-}$ groups are represented at left, labeled according to symmetry; the π orbitals of the dimer are numbered. Dashed lines showing interactions are given only for the π orbitals.

associated with magnetic ordering. Theoretical bases for this assertion can be found in ref 12.

We are aware that ferromagnetism is a complex phenomenon which certainly depends on electron correlation as well as other effects that are not explicitly considered in this work.¹³ We believe that a narrow, half-filled valence band is a necessary but not sufficient condition,¹² and we are merely trying to achieve this essential condition. Prediction of ferromagnetic behavior is a long, arduous journey and we are taking this path one step at a time.

Naturally, **1** itself cannot be incorporated into a polymer, due to a lack of connecting sites, so we will consider hypothetical derivatives of it. We first examine two simple, instructive model compounds before discussing the electronic structures of **1** and **2**. We then propose several candidate monomers for the hypothetical polymers and briefly discuss these and their corresponding dimers; they exhibit an interesting common electronic structure feature. Finally, we look at both planar and helical polymers of these systems; in these polymers we find some narrow, and some wide, half-filled valence bands. All calculations are performed using the extended Hückel method;¹⁴ parameters are listed in Appendix 2.

A Conceptual Model

All the five-membered rings we examine deviate extensively from ideal pentagonal symmetry, yet we can learn much about them from the starting point of a high-symmetry "parent" compound. We choose as the parent ring a system well-known to chemists, the so-called "Cp⁻" cyclopentadienide anion, $C_5H_5^-$.

The perfectly pentagonal Cp⁻ anion has the magic Hückel number of six π electrons. To make this system isoelectronic with the heterocycles, we add one more electron, thus arriving at the seven- π -electron moiety Cp²⁻. The π orbitals of this system are represented on the left side of Figure 1, as are the orbital energy levels for a ring with C-C = 1.40 Å. In this seven- π -electron ring, the e_2'' set has one electron in it.

The e_2'' orbitals are antibonding between carbons, so addition of the seventh π electron would result in C-C bond lengthening; it is likely also that a Jahn-Teller distortion would occur because one electron resides in

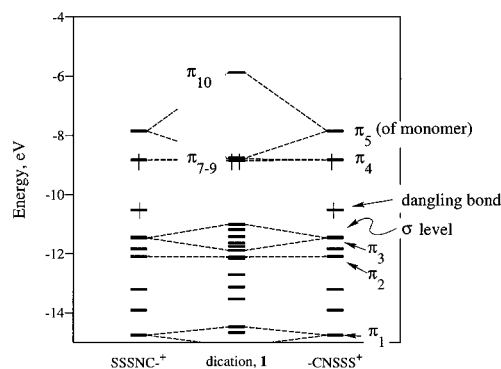


Figure 2. Orbital interaction diagram for two *cyclo*-CNSSS⁺ moieties, as in **2**, interacting to form the dication **1**. Important orbitals are labeled; dashed lines showing interactions are given only for the π orbitals.

a degenerate set of orbitals. We ignore those effects in our model; the heterocyclic systems of interest to us have other, stronger perturbations.

Now imagine connecting two of these idealized Cp²⁻ rings, removing two hydrogen radicals in the process, to arrive at a planar moiety with the stoichiometry $C_{10}H_8^{4-}$. The resulting π molecular orbital (MO) energy levels of this fulvalene-like anion are shown in the middle of Figure 1. Removal of one hydrogen atom from each ring causes a "dangling bond" to form on the corresponding carbon, which is the source for the σ orbitals of the components at about -11 eV in the figure. These move out of the valence region on forming the inter-ring bond.

The highest four π orbitals of the $C_{10}H_8^{4-}$ system are distinctly separate in energy from the lower six. These orbitals are derived almost exclusively from the e_2'' set: MO π_7 is 97.3% from the e_2'' set, π_8 and π_9 are each 100.0% derived from that set, and π_{10} is 94.7%. Thus, the a_1'' and e_1'' molecular orbitals do not to any significant degree interact with the e_2'' set upon the connection of two rings. Separation of the e_2'' -derived orbitals from the other π orbitals is a characteristic and important feature of the whole family of five-membered, seven- π -electron heterocycles and their derivatives.

The fourteen- π -electron $C_{10}H_8^{4-}$ anion appears to be a good candidate for a singlet ground state configuration, with the highest occupied MO being the doubly-occupied π_7 . Triplet states could arise from exciting one or both of the electrons from π_7 into orbitals π_8 and π_9 . Because we use a one-electron method of calculation, we cannot be certain what the ground state will be.¹² What we can say is that the energy splitting between MO π_7 and the MOs π_8 and π_9 will strongly affect the relative stability of the triplet and singlet states.

Does this construction apply to the Passmore system, **1**? Figure 2 displays the energy levels for a single *cyclo*-CNSSS⁺ ring, **2**, and for the dimer, both calculated using the experimental geometry of the dimer. An important qualitative similarity exists between the energy level pattern of *cyclo*-CNSSS⁺ and of Cp²⁻: the levels are split in a one-below two-below two pattern corresponding to the a_1'' - e_1'' - e_2'' orbitals of Cp²⁻. Likewise, the frontier π orbitals of the dimer split into a roughly two-below four-below four pattern as in $C_{10}H_8^{4-}$.

A significant difference between $C_{10}H_8^{4-}$ and **1** is the energy spread of the frontier orbitals, π_7 - π_9 . In the hydrocarbon, the splitting is 1.0 eV, whereas it is only 0.1 eV in **1**. From our one-electron method, we cannot

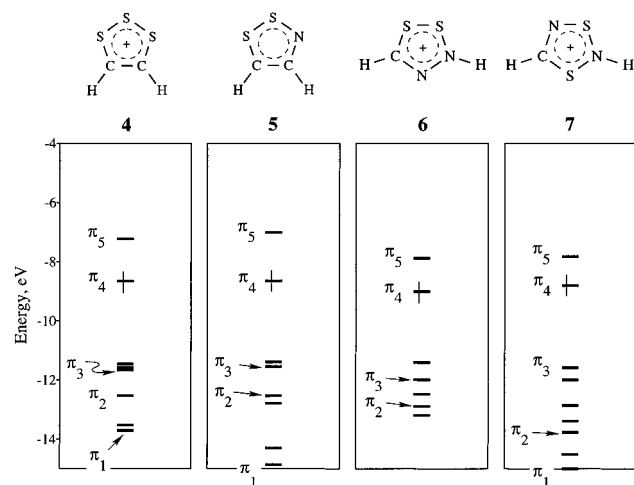


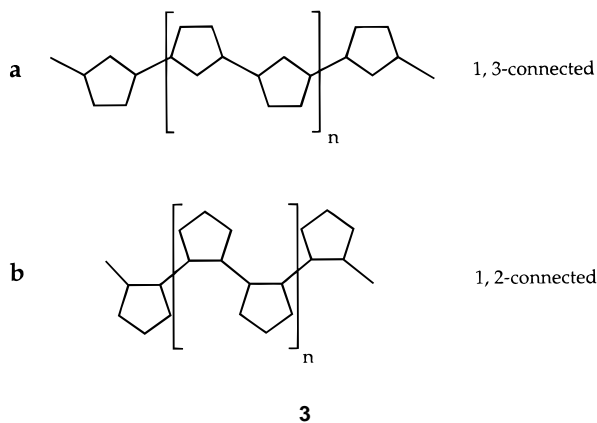
Figure 3. Energy level diagrams for heterocycles **4**–**7** (left to right).

say whether the small splitting of π_7 – π_9 will definitely result in a triplet ground state, though the results suggest that the singlet and triplet states in **1** are closer in energy than in $C_{10}H_8^{4-}$.

MP2 and Hartree–Fock configuration–interaction calculations by Caballol et al.^{15a} on an optimized geometry of **1** (optimized using two-configuration MCSCF for the singlet and OSRHF for the triplet, both with a 6-31G** basis) suggest that it has a triplet ground state, with a singlet–triplet splitting of 114.8 cm^{-1} (about 0.01 eV); Hartree–Fock calculations by Simkin agree with these results.^{15b} On the other hand, electron paramagnetic resonance experiments by Enright et al.² suggest that the ground state of **1** is actually a singlet but that a nearly degenerate triplet state exists, which is responsible for the observed room-temperature paramagnetism.

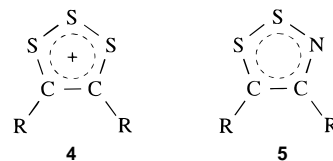
Monomers

Our goal is to design some potential high-spin polymers. The polymers we will study incorporate these heterocycles into their polymer backbone—they are not pendant groups. We will study a class of polymers of which there are two general structure types: **3a**, the 1,3-connected system, and **3b**, the 1,2-connected system.

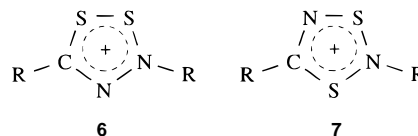


Connectivity at the 1,3-positions is found in many known polymers, such as polythiophenes¹⁶ and polythiazoles.¹⁷ However, the above geometries were inspired by the structure of **1**: if we were to make each of the nitrogen atoms in **1** three-coordinate, we arrive at

the 1,2-connected polymer; or, if we replace two of the sulfur atoms in **1** by three-coordinate atoms, we arrive at the structure of the 1,3-connected polymer. These maneuvers are easy to do “on paper” (their synthesis is much harder, we know...). We have chosen to study four different heterocycles for our purpose, the first two of which, depicted in **4** and **5**, are known experimentally.



We have also chosen to study two as-yet unknown members of the family, **6** and **7**. These two heterocycles



can (on paper, again) serve as monomers for the class of 1,3-connected polymers. Note that a heterocycle related to **7**, *cyclo*-(CR)SNSN, for which both nitrogen atoms are two-coordinate, is known.⁶

In calculations on all of these rings, we use the following bond lengths: S–S, 2.04 Å; C–S, 1.7 Å; N–S, 1.6 Å; C–N, 1.3 Å; N–N, 1.35 Å. The S–S bond length is a typical single bond, which is the distance observed in **1**, while all other distances more closely resemble lengths of partially conjugated bonds and are close to the values found in **1**.¹⁸ Bond angles are listed in Appendix 1.

Figure 3 shows the energy level diagrams for “monomers” **4**–**7**. In all of these seven- π -electron systems, the singly occupied MO π_4 is the highest occupied molecular orbital and is marked by a short vertical line.

What is remarkable about all of these systems is that, despite their obvious differences, all show a fairly clear 1–2–2 energy ordering of the π orbitals. In particular, the highest two π orbitals are distinctly higher in energy than the lowest three. These two orbitals we will denote as “ e_2'' -derived”, because they are closely related to the e_2'' orbitals of Cp^{2-} . To put it another way, the perturbation on the energy level pattern of massively substituting heteroatoms into the $C_5H_5^{2-}$ ring is not great.

The close resemblance in energy is *not* mirrored in the shapes of the wavefunctions for the molecular orbitals of these molecules. Figure 4 shows a representation of the wavefunctions for the crucial π_4 MO in each of the four heterocycles.

The π_4 orbitals for **4** and **5** are like one member of the Cp^{2-} e_2'' set and resemble each other qualitatively; the orbitals in **6** and **7** are like the other member of the Cp^{2-} e_2'' set (you can see this if you imagine that the line containing the C–H bonds in **6** and **7** corresponds to the nodal plane in the e_2'' orbital of Cp^{2-}), and they resemble one another. Appendix 2 contains a detailed perturbation–theoretical argument for why this should be so.

Compounds **4**–**7** all resemble **2** in that the energy splitting between their respective π_4 and π_5 orbitals is roughly of the same magnitude (1–2 eV). We might expect, therefore, a splitting pattern of the four highest π orbitals in the dimer of three below one, similar to

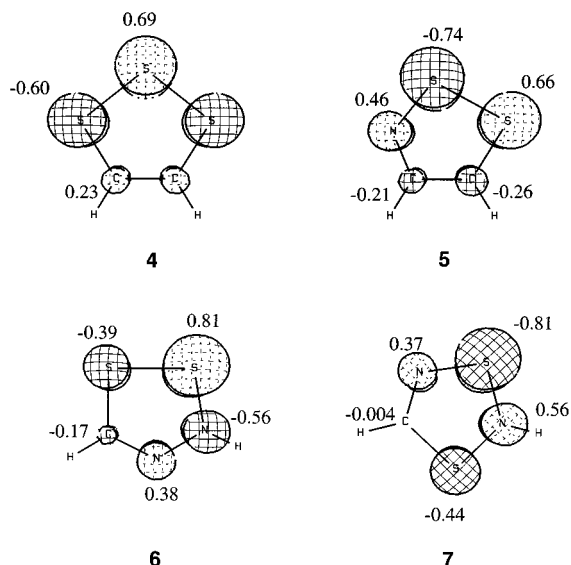
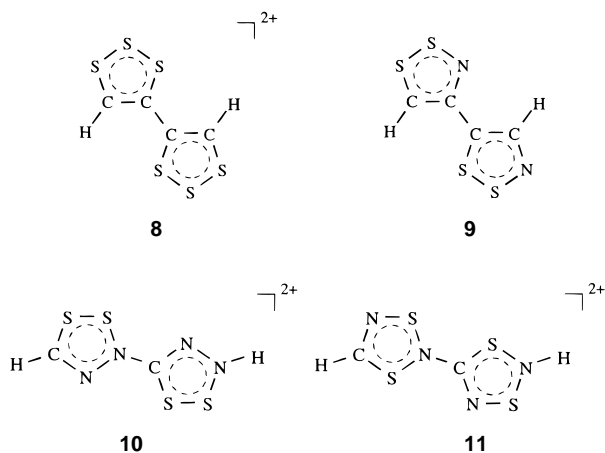


Figure 4. Representations of the HOMO, π_4 , for each of 4–7. Wavefunction coefficients are listed next to the corresponding icon.

the pattern in **1**; but as we will see, this is true only in the first two cases.

Dimers

Heterocycle **4** can give rise to only one possible dimer, but the other three rings each allow for three possible dimers. In those cases, we have arbitrarily chosen to study just that one permutation which does not have a center of inversion. Representations of the dimer structures are given in **8–11**.



None of these systems is known experimentally. We examine them here as a step in the path from monomer to polymer, because the electronic structures of these systems should give a hint as to what electronic properties we can expect in the extended systems.

Figure 5 shows the energy level diagrams for each of our dimers. In the 14- π -electron dimers the pattern of four orbitals arising from π_4 and π_5 of the monomer will be important. These levels (π_7 – π_{10}) determine whether the dimers can at least hope to have a high-spin ground state.

The similarity in the electronic structures of **8**, **9**, and **1** is readily apparent: all have a three-below one pattern of the frontier orbitals. The energy splitting of π_7 – π_9 for **8** and **9** is slightly larger than it is for **1**, yet it is still small enough to suggest that these dimers too

have a low-lying triplet state. Caballol et al. calculated the singlet–triplet gap of **8**, using the same method as they did in their calculations on **1**,¹⁵ and found the singlet to be more stable by only 120.3 cm^{-1} —about 0.01 eV; these results suggest that a significant fraction of molecules will be found in the triplet state at room temperature.

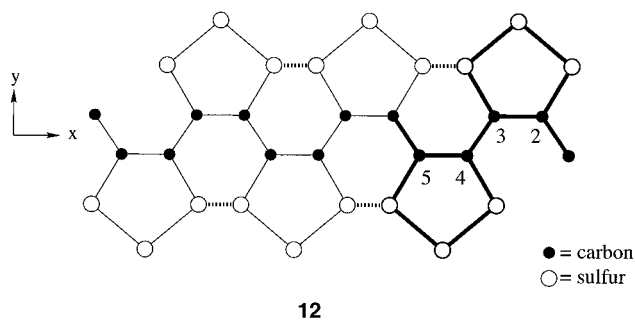
Should **8** and **9** be synthesized, we expect that they would display paramagnetic behavior at reasonably low temperatures. This also bodes well for the corresponding polymers, implying they too have a chance to be ferromagnetic.

Compounds **10** and **11**, however, display a somewhat different splitting pattern of the highest π orbitals. Having no relevant compounds to compare against, we cannot conclude anything about the singlet–triplet splittings, nor can we extrapolate to the polymer. We must simply calculate the hypothetical extended systems.

Polymers

From the previous section, we suspect that dimers of **4**, *cyclo*-(CR)SSS(CR), and **5**, *cyclo*-(CR)SSN(CR), have low-lying triplet states; dimers of **6** and **7** do not allow for easy extrapolation. We now examine hypothetical polymers of each of these systems in turn. In each case, the geometries of the heterocycles are identical to those used in 4–7 above; inter-ring angles are listed in Appendix 1.

Poly(cyclo-CSSSC⁺). Monomer **4** might form a polymer of the general structure **3a**; however, as we see in structure **12** as follows, it encounters steric trouble in a planar geometry. Atoms and bonds in the unit cell are outlined in bold; short intercell sulfur–sulfur contacts are shown by dotted lines. Black spheres represent carbon; white spheres are sulfur. For a C–C–C angle of 124°, the interring sulfur contacts, around 1.25 Å, are not physically realistic.



Rotating successive rings with respect to each other will make a more realistic polymer. This involves merely varying the C_2 – C_3 – C_4 – C_5 dihedral angle (which we denote as Θ_d) away from 180°, the planar conformation in **12**; successive dihedral angles are rotated in opposite directions. We thus make a helix out of the polymer.¹⁹

In all cases below, we exploit the screw axis symmetry of the helix to enable us to use the helical unit cell,²⁰ rather than any larger translational unit cell which may be present, for our calculations. Note that, for all of the polymers we examine, as the dihedral angle nears zero, each helix will start to squash such that every loop of the helix is very close to the loops above and below it (this is best seen with a model), resulting in a sterically crowded system. Ultimately, for $\Theta_d = 0^\circ$, the helix

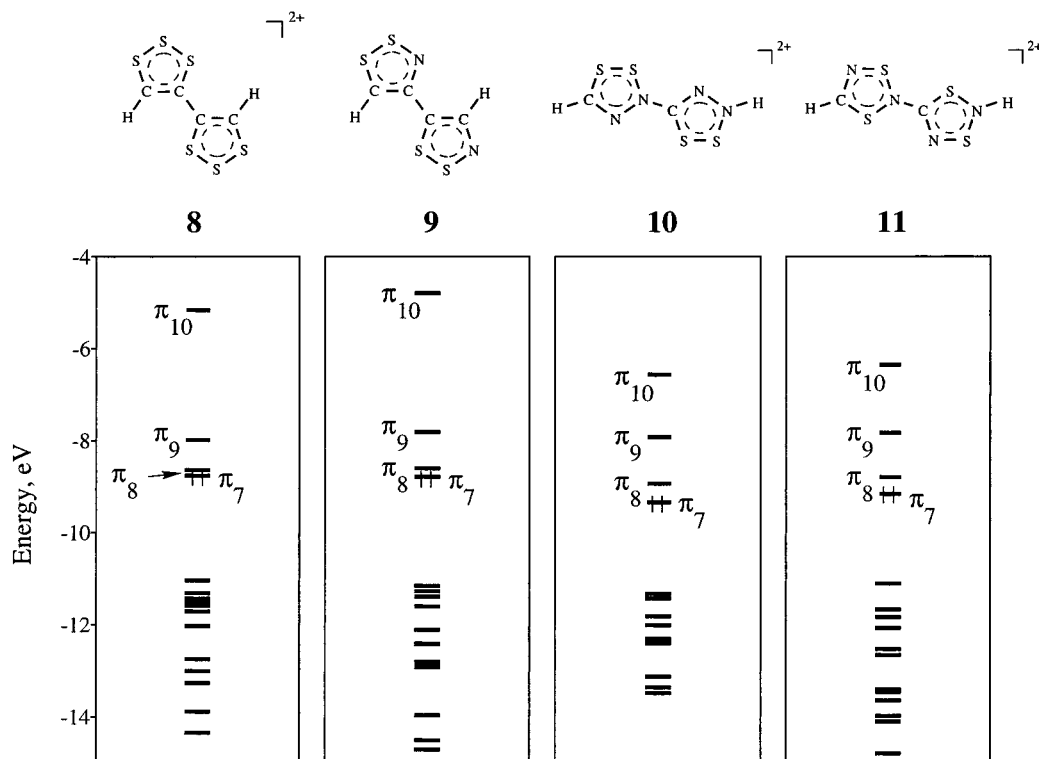


Figure 5. Energy level diagrams for dimers **8**–**11** (left to right). π levels are labeled.

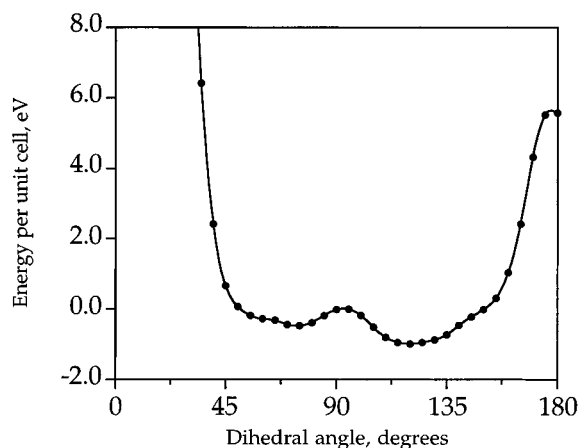


Figure 6. Total energy per (helical) unit cell of poly(*cyclo*-CSSSC⁺) as a function of dihedral angle. All calculated data are shown as black dots. Energies are given relative to the local maximum near 90°.

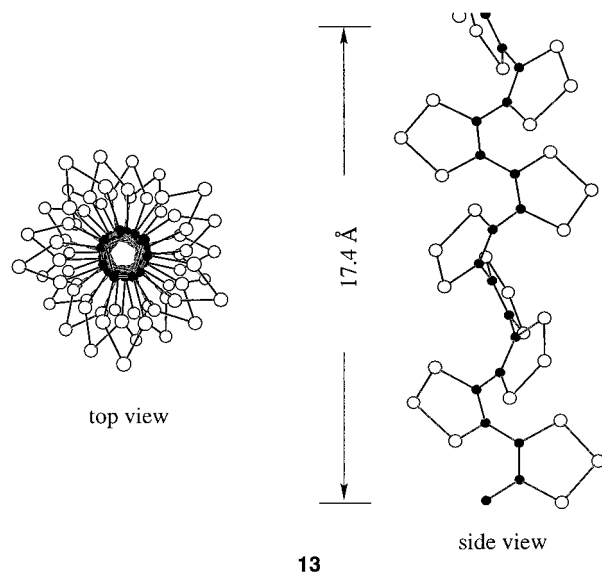
collapses into a single plane. The extreme dihedral angle of 0° is thus an unrealistic energy maximum.

Figure 6 displays the total energy of the polymer as a function of dihedral angle.

An important feature of this energy curve is the small peak near $\Theta_d = 90^\circ$. At this dihedral angle, the rings are oriented perpendicularly so that there is zero overlap between the π systems of nearest-neighbor rings (although π - σ mixing occurs). Because the inter-ring π interactions are stabilizing, the loss of overlap in this geometry results in an increase in total energy.

We find two energy minima, one at $\Theta_d = 74^\circ$ and another, the lowest energy conformation, at 120.4°. Its structure is given in **13**.

For this optimum geometry, Figure 8 shows the band structure calculated for the helical unit cell, which is simply *cyclo*-C₂S₃⁺. Throughout this paper we indicate the Fermi level as if the polymers in question were



metallic, with perfect spin-pairing. This is just a provisional convention, with no implication as to the true electrical and magnetic nature of the polymers.

The Fermi level cuts through a band which is isolated from the bands above and below it. This particularly flat valence band has a width of 0.29 eV; as mentioned in the introduction, such a narrow band is indicative of potential magnetic ordering.

Why is the valence band so narrow? To answer that, we first examine its composition. Valence and conduction bands are both π in character: at Γ , the highest occupied crystal orbital (HOCO, the valence band) is 99.2% π_4 in character (referring to orbital π_4 of the isolated monomer, **4**), while the lowest unoccupied crystal orbital (LUCO, the conduction band) is 92.1% π_5 ; at X, the HOCO is 98.8% π_4 and the LUCO 91.7% π_5 .

The bandwidth in the valence and conduction bands is proportional to the π overlap between rings.²⁰ This overlap is reduced when $\Theta_d = 120.4^\circ$, down to about half of what it would be in a planar system. The bandwidth is also proportional to the square of the carbon coefficient in its parent molecular orbital. Orbital π_4 (Figure 4) has a relatively small coefficient, 0.23, on carbon; this along with the decreased overlap is what causes the valence band dispersion to be so small.

The second energy minimum of this system, at $\Theta_d = 74^\circ$, lies 0.51 eV higher than the lowest energy minimum. For this dihedral angle, there are short non-bonded sulfur-sulfur contacts of 2.69 Å in the helix, between every fourth ring; third-nearest-neighbor rings are almost stacked directly on top of one another. This long contact significantly increases the bandwidth of the valence band (to 2.1 eV), which results in stabilization; it also increases dispersion of the other bands, a destabilizing process which competes against the first effect.²¹ The result is a shallow energy minimum.

Half-filled valence bands in one-dimensional systems often lead to Peierls distortions of the structure.²² A Peierls distortion of helical poly(*cyclo*-CSSSC⁺) will transform the system into an insulator or semiconductor, and it will involve a pairing of subunits. The most likely deformation we guess might be the pairing of rings in a face-to-face manner,¹ as seen in some crystal structures of related heterocycles, e.g., *cyclo*-(CR)SNS(CR),⁵ *p*-C₆H₄(*cyclo*-CNSNS)₂,²³ and S₂N₂CCN₂S₂.⁹ This in turn would involve putting "kinks" in the helix; it is likely a complicated geometrical distortion, and we do not consider it here or for any of the polymers discussed below. (Note, however, that pairing of seven- π -electron heterocycles in the solid state is observed only for neutral rings, not their cationic siblings such as (CR)-SSS(CR)⁺. Passmore and co-workers¹ suggest that electrostatics are responsible for the lack of pairing in **1**, which implies that the use of cationic heterocycles in a polymer may be a good strategy for avoiding this distortion.)

To sum up the results for poly(*cyclo*-CSSSC⁺), we calculate that this system has two energy minima for helical conformations: one at a C-C-C-C dihedral angle of 74° and one at 120.4° . The 120.4° isomer is the lowest energy minimum; it has an electronic structure characterized by relatively flat bands, closely related to the levels of the monomer *cyclo*-(CR)SSS(CR) ring, **4**. In particular, the valence and conduction bands are almost pure π_4 and π_5 in character, respectively. The valence band is half-filled and very narrow, which can be ascribed to the effects of decreased intercell overlap and a small coefficient in π_4 on carbon. This isomer shows promise for being a ferromagnetic system.

It is worthwhile to reemphasize here that we are pursuing the simplest criterion for potential ferromagnetic ordering: a narrow valence band. We are very well aware that consideration of electron exchange is essential and that our simplistic one-electron picture does not include this. A narrow, half-filled band can lead to ferromagnetic ordering, but it can also give rise to Peierls-distorted diamagnetic structures or antiferromagnetic insulators as well, as a reviewer has quite correctly noted. What we offer is a start, based on a promising heterocyclic structural unit.

To find further promising polymers (i.e., those having a narrow, half-filled valence band), we seek heterocycles related to **4** which might have a still smaller coefficient

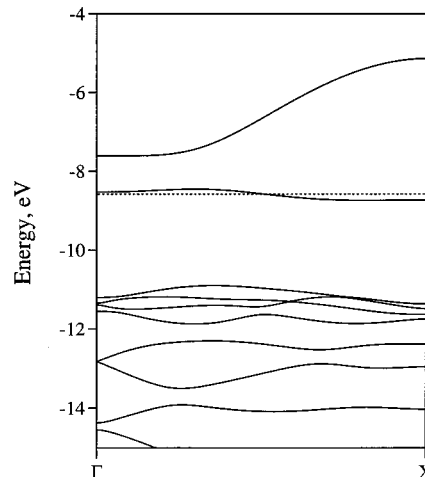
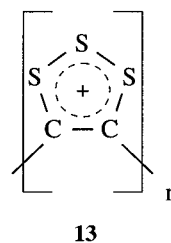


Figure 7. Band structure of poly(*cyclo*-CSSSC⁺), **13**, in its minimum energy helical conformation ($\Theta_d = 120.4^\circ$; see **13**). The Fermi level is indicated with a dotted line.

on carbon in their highest occupied π orbital. To effect this strategy, we need to substitute atoms for sulfur which are less electronegative or atoms for carbon which are more electronegative, which forces the orbitals π_4 and π_5 to be more concentrated away from the carbon atoms. Selenium, one possible alternative to sulfur, has about the same electronegativity, but preliminary calculations suggest that it will not lead to smaller carbon coefficients in the HOMO; we have not explored whether tellurium might be useful.

poly(*cyclo*-CSSNC). Substituting more electronegative atoms for sulfur will have the opposite effect, resulting in carbon coefficients which are less favorable for a narrow valence band. However, the monomer *cyclo*-(CR)SSN(CR), **5**, is experimentally known, and the substitution of only one atom is a small perturbation; thus we have chosen to study it.

As with poly(*cyclo*-CSSSC⁺), steric interactions force the polymer away from its planar conformation. The basic shape of the potential energy curve is similar to Figure 6: steric constraints at $\Theta_d = 0$ and 180° result in energy maxima; near $\Theta_d = 120^\circ$ each ring is relatively distant from its neighbors, and hence, there is an energy minimum at 125° . The band structure for this minimum energy conformation is quite similar to that shown in Figure 7 for poly(*cyclo*-CSSSC⁺); the valence band dispersion is only 0.32 eV. Overall, this polymer is very similar to poly(*cyclo*-CSSSC⁺); it has a marginally wider valence band and is about as likely to display magnetic ordering.

Poly(*cyclo*-CSSNN⁺). The next hypothetical polymer we examine is a *meta*-linked one, derived from (CR)SS(NR)N⁺, heterocycle **6**, and has the general connectivity depicted in **3b**. Although **6** itself is not yet experimentally known, we consider it a promising monomer, because in addition to being closely related to the known *cyclo*-(CR)SSS(CR)⁺, **2**, our calculations

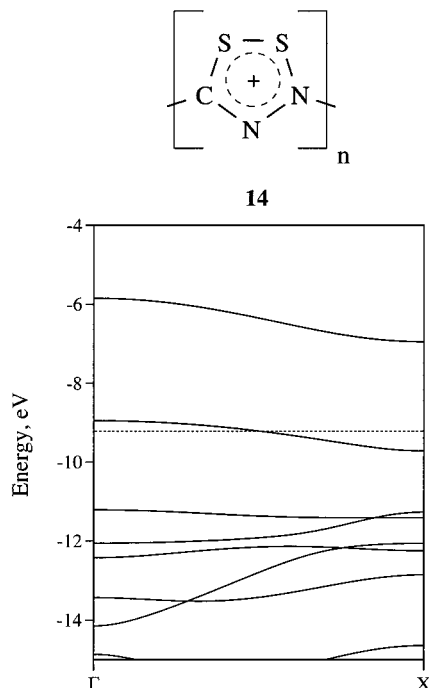
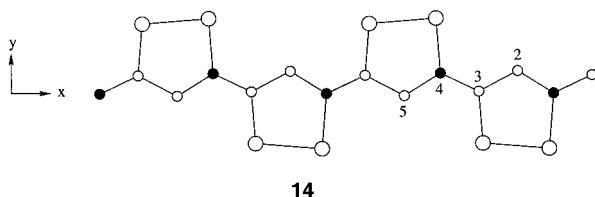


Figure 8. Band structure of planar poly(*cyclo*-CSSNN⁺), **14**, in its minimum energy conformation ($\Theta_d = 180^\circ$). The Fermi level is indicated with a dotted line.

(see Figure 4) indicate that its HOMO has a small coefficient on carbon, which could lead to a narrow band in the polymer.

In the polymer we consider, the geometry of each ring is identical to that in **6**. A planar conformer is shown in **14** as follows. Small black circles represent carbon (e.g. the atom labeled 4), small light ones are nitrogen (atoms 2, 3, and 5), and large white circles are sulfur.



In contrast to the first two polymers, this one does not suffer from steric repulsion in a planar conformation; the shortest inter-ring sulfur-sulfur distance is 4.9 Å. The band structure of the planar polymer is shown in Figure 8; once again we have used the helical unit cell of stoichiometry *cyclo*-CN₂S₂⁺.

The electronic structure of this polymer is characterized by fairly flat bands and a half-filled highest-occupied band which is isolated from those above and below it. However, the dispersion of the valence band, 0.77 eV, is more than twice that found in the low-energy conformations of the first two polymers, suggesting that this system is not as likely to display magnetic ordering.

In contrast to poly(*cyclo*-CSSSC⁺) and poly(*cyclo*-CSSNC), this polymer displays strong conjugation in its π system; mixing between orbitals is significant. The HOCO at Γ is 77.6% π_4 (where π_4 refers to the orbitals of the monomer, **6**) and 21.0% π_5 , and at X , it is 84.7% π_4 and 14.5% π_5 . Likewise, the lowest unoccupied band is mainly π_5 with a significant fraction of π_4 character mixed in. Although mixing between the highest two bands is strong, those e_2'' -derived orbitals mix almost

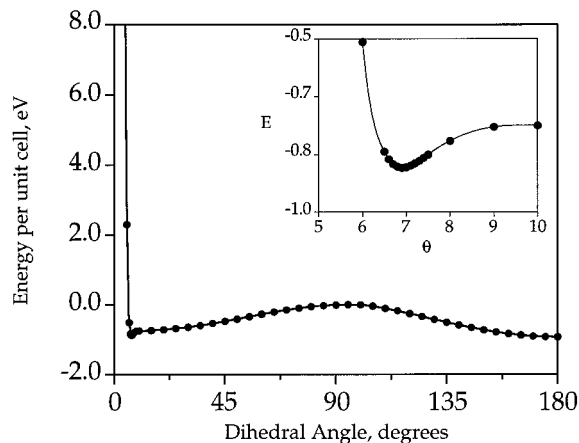
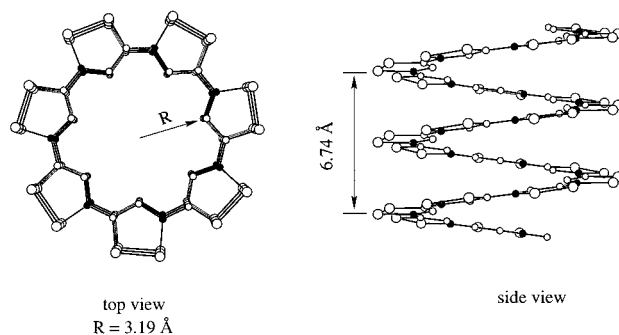


Figure 9. Total energy per (helical) unit cell of poly(*cyclo*-CSSNN⁺) as a function of dihedral angle. Energies are given relative to the local maximum near 90° . The inset at upper right is a blowup of the region at a small dihedral angle, where the second-lowest energy minimum occurs.

exclusively with each other, and not with the other π orbitals, proving yet again how the e_2'' -derived orbitals are distinct.

To find a conformer with a narrow valence band, we would need to distort the polymer away from planarity toward a helix, which will reduce intercell π overlaps and thus the bandwidth. However, very strong π conjugation between rings makes this distortion energetically unfavorable. As Θ_d approaches 90° , the energy rises by about 1 eV relative to $\Theta_d = 180^\circ$, due to the breaking of π conjugation; Figure 9 shows the energy of this polymer as a function of dihedral angle.

At $\Theta_d = 7^\circ$, there is a sharp dip in the potential energy curve due to favorable long-range interactions between rings as the helix starts to compress. Long sulfur-sulfur contacts (3.37 Å at $\Theta_d = 7^\circ$) result in a significant overlap between π orbitals of seventh-nearest-neighbor rings (**15** shows two views of this conformer), which broadens the half-filled valence band and subsequently stabilizes the polymer.



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As the dihedral angle decreases from 90° , the local geometry around each ring approaches planarity; thus π conjugation is restored. For Θ_d greater than about 9° , the next loop of the helix is still beyond a van der Waals contact (which is ~ 3.6 Å for sulfur atoms), so no long-range interactions are present.

Once the dihedral angle decreases enough for the rings to get within a van der Waals contact distance, the π orbitals of each ring interact in a σ fashion along the helical axis. The effect lends greater bandwidth to the π orbitals, particularly the frontier bands, making

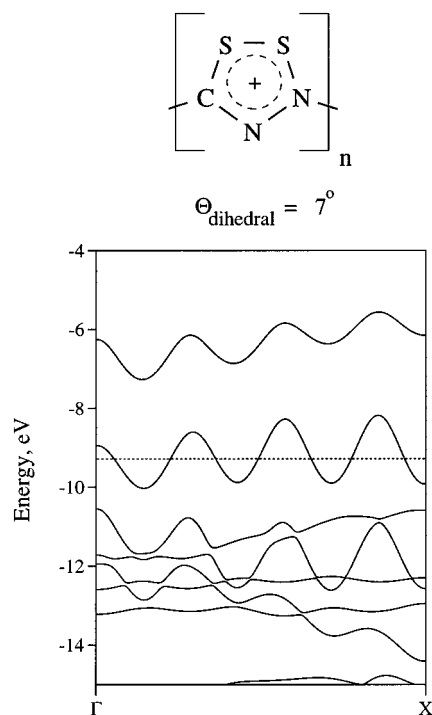


Figure 10. Band structure of poly(*cyclo-CSSNN*⁺) in its helical minimum energy conformation ($\Theta_d = 7^\circ$). The Fermi level is indicated with a dotted line.

them “wavy”, as seen in Figure 10; it is this waviness in the valence band which provides the stability for a helical conformer at $\Theta_d = 7^\circ$.

Unfortunately, the most stable conformers of this system—at $\Theta_d = 7$ and 180° —have fairly wide frontier bands, and those conformers with narrow bands (around 90°) are very unstable relative to those with wide bands. We do not expect this system to provide interesting magnetic behavior, although it could be conducting. Or it might undergo a symmetry-lowering Peierls distortion.

How might these results suggest to us a better “design” for a promising magnetic polymer? As long as the polymer is most stable in a planar conformation, mixing between π_4 and π_5 will be strong and the bandwidth of the highest occupied band will depend on it. To reduce this mixing, we need (1) monomers in which π_4 and π_5 are farther apart in energy, which would in general reduce the mixing, and (2) among those, we need systems with small coefficients on the three-coordinate atoms in the highest filled MO.

poly(*cyclo-CSNSN*⁺). The final polymer system we examine is based on monomer 7. This as-yet unknown ring has the very promising feature that, although π_4 and π_5 are not very far apart in energy, its π_4 orbital has a nearly zero coefficient on carbon (see Figure 4), suggesting that it will give rise to a narrow half-filled band.

The band structure of a planar conformation, having the general connectivity of type **3b**, is shown in Figure 11.

The electronic structure is very similar to that of poly(*cyclo-CSSNN*⁺), **14**: most bands, especially the frontier bands, are quite flat; the highest occupied and lowest unoccupied bands are pure π in character; those bands are also mainly π_4 and π_5 , and much mixing has occurred between them but not with the other π bands. In particular, the valence band has a dispersion of 0.34

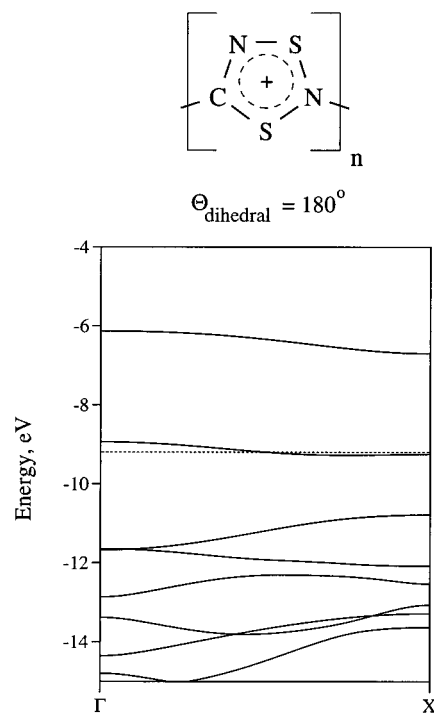


Figure 11. Band structure of poly(*cyclo-CSNSN*⁺) in its planar conformation ($\Theta_d = 180^\circ$). The Fermi level is indicated with a dotted line.

eV, which is comparable to that in poly(*cyclo-CSSSC*⁺) and poly(*cyclo-CSSNC*) at their respective minima.

The narrow bandwidth of this isomer is directly attributable to the small coefficient on carbon in π_4 . Recall that another factor in determining bandwidth is the intercell overlap; we can reduce that overlap by forcing the polymer to become helical. Indeed, at dihedral angles of 120 and 90° , we calculate bandwidths of 0.091 and 0.097 eV, respectively, for the half-filled valence band. But, as with all the other polymers we have examined, the intercell π interaction is favorable; thus, rotation of the rings toward $\Theta_d = 90^\circ$ is destabilizing.

The $\Theta_d = 90^\circ$ isomer is about 0.56 eV per unit cell less stable than the planar $\Theta_d = 180^\circ$ isomer. In this regard, and also in the general shape of the energy-versus-dihedral angle curve, poly(*cyclo-CSNSN*⁺) is very similar to poly(*cyclo-CSSNN*⁺); this results from their very similar geometries. The conformation with the smallest valence band dispersion is not the most stable.

An interesting difference between this polymer and poly(*cyclo-CSSNN*⁺) is that the helical minimum, at $\Theta_d = 2^\circ$, is more stable than the planar minimum. The difference is small—0.08 eV per unit cell—but it does suggest that a fat, tubelike helical conformation is likely. As with the helical poly(*cyclo-CSSNN*⁺), this conformation is characterized by stabilizing long-range interactions between π orbitals of (thirteenth-nearest-neighbor) rings. Here again, there are important S–S contacts (3.5 Å, which, though extremely long, are important),²⁴ the helical radius is large, and nearest neighbors are practically planar with respect to each other. Again, we find waviness in the π bands, each having seven maxima and seven minima; the bandwidth of the valence band for this conformation is 1.2 eV.

Conclusions

The polymers, and some of the monomers, examined here are hypothetical, and thus, the results must be

taken with a grain of salt; nonetheless, we have what we believe are important and generally valid conclusions. In these seven- π -electron monomers and their oligomers, the e_2'' -derived π orbitals are unique; they mix very little with other orbitals even after significant perturbation to the geometry of a ring (by heteroatom substitution, or dimerization) or of a polymer (by breaking planarity to form helices). This feature of the e_2'' -derived orbitals is characteristic of the whole family of five-membered, seven- π -electron heterocycles for a wide range of compositions.

Knowing that these heterocycles all have this commonality, we then tried to exploit their differences. They have a wide range of coefficients in their e_2'' -derived molecular orbitals; thus, we examined how the heterocycles interact with each other in dimer and polymer form, in order to try to theoretically design a polymer which might be ferromagnetic.

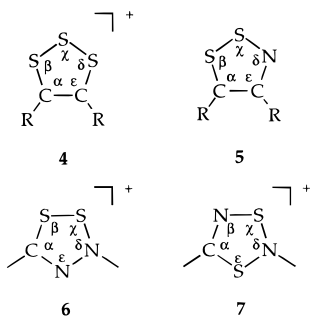
We found two hypothetical helical polymers, poly(*cyclo*-CSSSC⁺) and poly(*cyclo*-CSSNC), and one planar, poly(*cyclo*-CSNSN⁺), with valence bandwidths of approximately 0.3 eV. In the first two cases, the small valence band dispersion is due to a combination of two effects: (1) the nonplanarity reduces π overlap between neighboring rings, and (2) the coefficients on those atoms which connect rings are small in the HOMO of the monomer. In the planar polymer, the narrow valence band arises because of an extremely small coefficient on carbon in the monomer HOMO.

One can envision many extensions of this work, involving different heterocycles and different connectivity in polymers. We believe that this variety allows for tailoring physical properties in a rational and systematic manner. Hopefully the experimentalists will prove us right. Or wrong.

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Appendix 1: Geometries

For heterocycles 4–7, the angles we chose are labeled as follows by Greek letters.



The values for these angles are

	4	5	6	7
α	120.497	120	117.628	120
β	99.503	90	90	114.083
χ	100	96.760	99.061	95
δ	99.503	121.844	113.311	122.305
ϵ	120.497	111.395	120	88.612

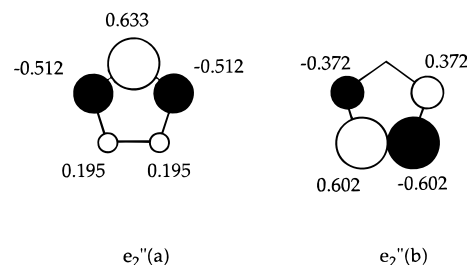
Inter-ring angles in the polymers are as follows: poly(*cyclo*-CSSSC⁺), all C–C–C angles = 124°; poly(*cyclo*-CSSNC), all C–C–C angles = 123.1°; poly(*cyclo*-CSSNN⁺), N₂–N₃–C₄ = 126.7° and N₃–C₄–N₅ = 122.4° (cf. 14); poly(*cyclo*-CSNSN⁺), angle S–C–N = 121.5° and angle C–N–S = 120.1°.

Appendix 2

Rationalizing the π_4 Orbital Shapes. As seen in Figure 4, two of the monomers we analyzed, 4 (*cyclo*-CSSSC⁺) and 5 (*cyclo*-CSSNC), have a highest occupied orbital which is shaped like one of the well-known e_2'' set in Cp[−]; the other two monomers, 6 (*cyclo*-CNNSS⁺) and 7 (*cyclo*-CSNSN⁺), have a highest occupied orbital shaped like the other member of the e_2'' set of Cp[−]. We can understand the shapes of the frontier orbitals in our monomers by use of simple Hückel theory (SHT) and perturbation analysis. In this appendix, we will examine in detail the frontier orbitals of 4 (*cyclo*-CSSSC⁺) and 7 (*cyclo*-CSNSN⁺) in order to explain why they have this difference.

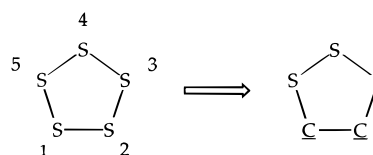
SHT uses two types of parameters, α and β , and understanding a perturbation analysis²⁵ requires understanding their physical meaning: α_z is a measure of electronegativity for atom z, and β_{yz} is a measure of the strength of (π) interaction between atoms y and z. (Note that both have dimensions of energy, and the value of β is unspecified but negative.) By convention, $\alpha_C = \alpha$ and $\beta_{CC} = \beta$. We have chosen $\alpha_N = \alpha + 0.5\beta$ and $\alpha_S = \alpha$ to reflect the relative electronegativities of sulfur, nitrogen, and carbon. For their interaction parameters, we choose $\beta_{NC} = \beta$, $\beta_{NS} = 0.7\beta$, $\beta_{SS} = 0.6\beta$, and $\beta_{CS} = 0.8\beta$ (which reflect the magnitude of π -type overlap between p orbitals on the corresponding atoms).

Our perturbation analysis uses a hypothetical planar S₅³⁺, equivalent to that of the well-known Cp^{2−} group, as its starting point. S₅³⁺ has an e_2'' set of orbitals shaped almost exactly like those in the e_2'' set of Cp^{2−} (see Figure 1). The e_2'' set has an SHT-calculated energy of -0.971β and the following coefficients: Note



how we have labeled the orbitals $e_2''(a)$ and $e_2''(b)$ for clarity. We are going to examine what happens to the coefficients and energies of these orbitals as the atoms in the ring are “perturbed” to become the atoms in heterocycles 4 and 5.

The first perturbation “path” we examine is for 4:



We simply replace two of the sulfur atoms (labeled 1 and 2) by carbon atoms in one step. This gives rise to the following perturbation terms in the SHT Hamiltonian:

$$\Delta\beta_{12} = 0.4\beta$$

$$\Delta\beta_{23} = 0.2\beta$$

$$\Delta\beta_{51} = 0.2\beta$$

$$\text{all } \Delta\alpha = 0$$

The general formula for the first order correction to the energy of an orbital (see Heilbronner and Bock²⁵) is

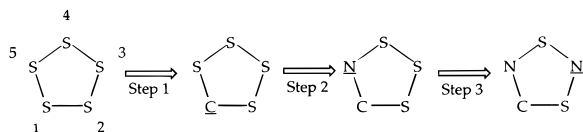
$$\Delta E = \sum_{\text{atoms } i} c_i^2 \Delta\alpha_i + \sum_i \sum_j c_i c_j \Delta\beta_{ij}$$

where c_i is the coefficient in this particular molecular orbital on atom i . This gives us a good idea of what effect each perturbation will have: if $\Delta\beta$ is a positive multiple of β (increased interaction) and if the coefficients involved have opposite signs, the energy of the orbital is raised. For electronegativity perturbations, regardless of the sign of the coefficient on the atom being perturbed, a change to a more electronegative atom lowers the energy of the orbital and vice versa for change to a less electronegative atom.

In this particular perturbation, we must use degenerate first-order perturbation theory, which, although mathematically more complicated than the nondegenerate case, leads to reasoning quite similar to that outlined above. We calculate ΔE for $e_2''(\text{a})$ of -0.049β and ΔE for $e_2''(\text{b})$ of -0.468β , resulting in first-order corrected energies of -1.020β and -1.439β , respectively. Stepping back from the calculations and using our interpretation of the two SHT parameters, we find that what we have done in the course of this perturbation is to increase the "interaction parameter", β , for three bonds. Looking at the shape of orbital $e_2''(\text{b})$, we note that it has antibonding interactions across all three of those bonds and that the two atoms which are made carbons have very large contributions (coefficients are ± 0.602). This means that the antibonding character of the MO is increased and thus it is only natural that the energy should increase. For orbital $e_2''(\text{a})$, the coefficients on the atoms which are perturbed toward carbon are small ($+0.195$), and there is a mix of bonding and antibonding interactions going on. Thus, we do not expect this orbital to rise much in energy as a result of the perturbation.

Indeed, an "exact" SHT calculation (i.e., diagonalizing the Hückel matrix) gives us energies of -1.022β and -1.443β for the $e_2''(\text{a})$ -like and $e_2''(\text{b})$ -like orbitals, respectively, which are quite close to the perturbation-derived values. We feel, then, that we understand why the HOMO of **4**, *cyclo-CSSSC*⁺, has the shape of $e_2''(\text{a})$: simply because the increased overlap of carbon-carbon and carbon-sulfur π bonds relative to that of sulfur-sulfur π bonds leads to stronger antibonding in $e_2''(\text{b})$, which raises it in energy relative to $e_2''(\text{a})$.

To explain the orbitals of heterocycle **7** we require a longer perturbational path. This is because a perturbation of carbon or sulfur to nitrogen is actually quite large and it is not reasonable to change more than one atom per step:

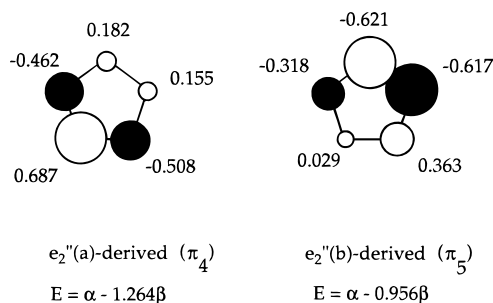


Step 1. We orient the e_2'' orbitals of S_5^{3+} such that the "unique" atom is atom no. 1; this is possible because of the degeneracy of the two orbitals. Now change atom no. 1 from sulfur to carbon. Orbital $e_2''(\text{b})$ will not change at all in energy, because the coefficient of atom no. 1 is zero in this case—in other words, atom no. 1 does not contribute to the orbital, and thus any changes in that atom will not affect the orbital.

As for $e_2''(\text{a})$, note that our perturbation involves only the terms $\Delta\beta_{12} = 0.2\beta$ and $\Delta\beta_{51} = 0.2\beta$. We increase the interaction for the bonds between atoms 1 and 2 as well as atoms 1 and 5. Both those interactions are antibonding; thus, we expect the $e_2''(\text{a})$ -like orbital to rise in energy. Indeed, our perturbation theory calculations give energies corrected to first order of -0.971β , and -1.230β for $e_2''(\text{b})$ and $e_2''(\text{a})$, respectively. Exact SHT calculations give -0.971β and -1.234 , respectively.

Step 2. Change atom no. 5 from sulfur to nitrogen. This puts three terms in our perturbation Hamiltonian: $\Delta\alpha_5 = 0.5\beta$, $\Delta\beta_{51} = 0.2\beta$, and $\Delta\beta_{54} = 0.1\beta$. The $\Delta\alpha$ term reflects a change in electronegativity and contributes a stabilization to the first-order energy change: $(c_5^2)(\Delta\alpha_5) = (c_5^2)(0.5\beta) < 0$ (recall that β in SHT is a negative number).

Nitrogen-carbon and nitrogen-sulfur $p-\pi$ orbitals have better overlap than sulfur-carbon and sulfur-sulfur $p-\pi$ orbitals, hence the increase in interaction parameters. The coefficients in orbitals π_4 and π_5 (numbered according to energy, π_5 the highest), however, are antibonding, so that the interaction perturbations contribute destabilizing terms to the change in energy for each MO. We anticipate, then, that the MOs do not change much in energy. Indeed, calculations reveal this to be true:



Note that the shapes of the wave functions also do not change much as a result of substituting N for S. π_4 still has the character of $e_2''(\text{b})$, although the loss of symmetry in the molecule means that the carbon coefficient need not be (and is not) zero.

Step 3. This step is similar to step 2, because again we substitute a nitrogen atom for a sulfur, and again, the electronegativity perturbation "tries" to stabilize the two frontier π orbitals, while the interaction parameter perturbation tries to destabilize them. The net result is not much change. Since atom 3 contributes a great deal to orbital π_4 as reflected in its coefficient of -0.617 , we expect the electronegativity perturbation (which goes as $0.5\beta \times 0.617^2$) to have a larger effect on this orbital than the interaction parameter perturbations (which go as $2(0.1\beta)(-0.617)(0.621)$ and $2(0.1\beta)(-0.617)(0.363)$). Orbital π_5 has a small contribution from atom 3 and thus is expected to not change much in energy.

Perturbation theory calculations reflect these expectations: the calculated energies of π_4 and π_5 for the final molecule are -0.887β and -1.262β , respectively. The

Table 1. Parameters Used in Extended Hückel Calculations

atom	orbital	H_{ii} (eV)	ζ
C	2s	-21.4	1.625
	2p	-11.4	1.625
N	2s	-26.0	1.950
	2p	-13.4	1.950
S	3s	-20.0	2.122
	3p	-11.0	1.827

exact SHT calculations give -0.910β and -1.263β , respectively.

This system is greatly perturbed from the initial S_5 ring, but through the perturbation theory analysis we gain some insight into why the frontier orbitals are shaped the way they are. The largest influence in this path is that of substituting carbon for sulfur in the first step. This "polarizes" the orbitals by providing a 2-fold axis; it also pushes up the $e_2''(a)$ orbital in energy because of increased interaction parameters for the two C-S bonds. The next two steps—substitutions of nitrogens for sulfurs—seem like they should have even greater influence; that they do not is a result of competing factors. Stabilization due to increased electronegativity is offset by destabilizations due to increased interaction parameters. Note that this does not preclude the shapes of the wave functions changing, and they do actually mutate away from the e_2'' forms—but not very far. That is a result of the energy separation between π_4 and π_5 caused by the carbon substitution, which makes second-order mixing between the orbitals less important.

Appendix 3: Extended Hückel Parameters

Extended Hückel computations were performed using the packages YAeHMOP,²⁶ CACAO,²⁷ and NNEW3.²⁸ A weighted H_{ij} was employed, as were the atomic parameters (H_{ii} , orbital energy, ζ , Slater exponent) given in Table 1. A 100 k -point set was used for average properties calculations.

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