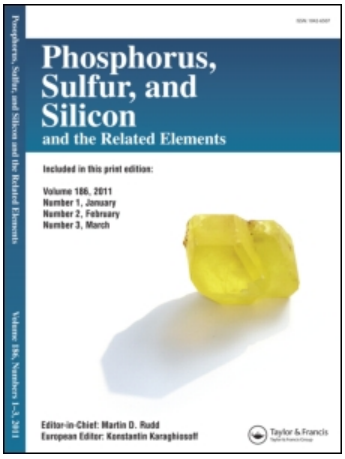

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A MOLECULE LIKE SODIUM

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The use of neutral π-radicals as building blocks for molecular conductors holds both appeal and challenge. Such systems obviate the need for counterions, as charge transfer is not required to generate charge carriers. Essentially an array of π-radicals should function like atoms in an elemental metal, e.g., sodium, affording a half-filled energy band. Most radicals, however, tend to dimerize, and even when association can be suppressed the resulting low bandwidth W*, coupled with a high on-site Coulomb repulsion* U*, leads to a Mott insulating state. We are pursuing the design and synthesis of stable heterocyclic thiazyl radicals, with a view to generating stable, crystalline materials with a high* W/U *ratio. The search for these new radicals, the molecular analogues of sodium, is the subject of this presentation.*

Keywords: Conductivity; electrochemistry; heterocycle; magnetism; neutral radical; solid state structures; sulfur-nitrogen

For over 30 years the development of organic conductors, both molecular and polymeric, has relied almost exclusively on the use of charge transfer (CT) to generate charge carriers.[1] Accordingly, conductive systems have required two components, i.e., a donor and an acceptor, although both can be incorporated into a single molecule.[2] An alternative to the CT paradigm is to use neutral π-radicals as the building blocks for a single component molecular material. In an ideal neutral radical conductor (NRC) material the stacked array of radicals, each with one

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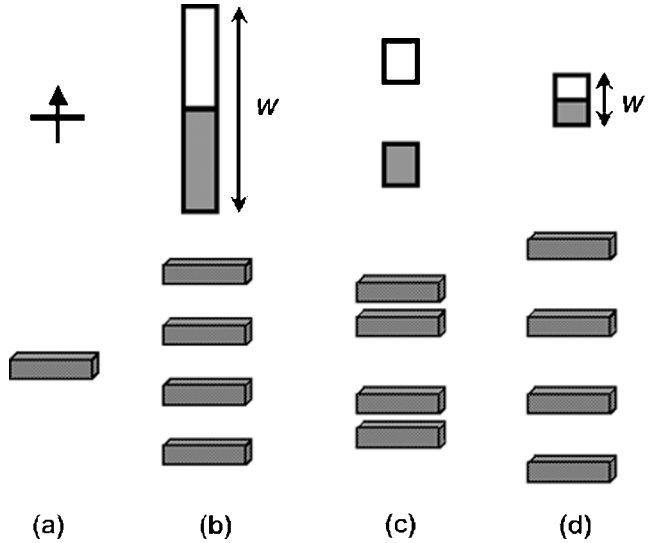


FIGURE 1 Energy levels and bands associated with (a) a single π-radical, (b) an idealized stack of strongly interacting π-radicals ($W > U$), (c) a Peierls distorted π-radical stack, and (d) a weakly interacting array of π-radicals ($W < U$).

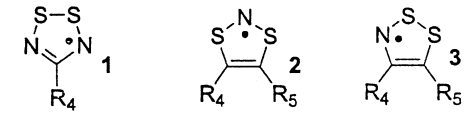
unpaired electron (Figure 1a), would function like atoms in an elemental metal[3] and, based on a simple band model of electronic structure, the bulk material would possess a half-filled energy band (Figure 1b), as in elemental sodium.

There are, however, several shortcomings to this model. First, any 1-dimensional half-filled energy band is prone to a Peierls instability, i.e., the radicals will associate into closed shell dimers (Figure 1c).[4] Second, if dimerization can be suppressed, e.g., by steric bulk, the resulting low electronic bandwidth W, coupled with the high on-site Coulomb repulsion energy U associated with a half-filled band, leads to a Mott insulating state (Figure 1d).[5] Essentially the spins are trapped on the radicals and, while interesting magnetic interactions can be observed,[6] charge transport is suppressed.

Improved conductivity in NRCs thus requires materials with systems with a large bandwidth W and a small on-site repulsion U, i.e., a high W/U ratio, and considerable progress has been made using organic, phenalenyl-based radicals.[7] The thrust of our work, however, is on the use of inorganic radicals based on heterocyclic thiazyl/selenazyl frameworks.[8] While the a priori estimation of the magnitude of both W and U for these systems is not practical, trends in the gas phase

disproportionation enthalpies ΔH_{disp}* for a series of related radicals provide a working mirror to the trends in U. A limited database of experimentally obtained ionization potentials has been compiled,[9] and reliable estimates of both *IP* and *EA* values can now be obtained easily by computation.[10,11] Alternatively, solution based cell potentials E_{cell}, when accessible by experiment, can be used as an indirect measure of U.[12] Using either criterion, the working prescription for good conductivity requires making radicals with good ion energetics, i.e., low ΔH_{disp} and E_{cell} values.

From a structural perspective the radicals must not dimerize in the solid state, and yet should display strong intermolecular interactions, so that sufficient electronic bandwidth W is generated to offset the on-site Coulomb barrier U. Understanding, however, let alone controlling the way heterocyclic radicals interact in the solid state poses a major challenge. Crystal engineering[13] methods hold much appeal, and the use of supramolecular synthons[14] to dictate architecture has enjoyed a degree of success,[2d,15] but the task of establishing structure-property relationships remains largely empirical. The design of new materials thus begins with the identification and exploration of thermally stable radical systems that can be easily modified, both structurally and electronically.



1,2,3-5-DTDA **1,3,2-DTA** **1,2,3-DTA**

Dithiazolyl Radicals—Ion Energetics

Much of our early work on neutral radical conductors focused on 1,2,3,5-dithiadiazolyl (DTDA) radicals **1**,[9] but these materials suffered from rather large ΔH_{disp} and E_{cell} values regardless of the nature of the 4-substituent.[16] By contrast the redox properties of 1,3,2- and 1,2,3-dithiazolyl (DTA) radicals **2** and **3** can be significantly modified. While simple monofunctional DTA derivatives have relatively large disproportionation energies, the incorporation of spin reservoirs at the 4,5-positions can be used to reduce both ΔH_{disp} and E_{cell} values.

*ΔH_{disp} is the enthalpy change for the conversion of two gas phase radicals R into a cation/anion pair, i.e., 2 R $\leftrightarrows$ $R^+ + R^-$, and accordingly is equal to the difference between the ionization potential (*IP*) and electron affinity (*EA*). The solution based cell potential $E_{cell} = E_{1/2}(ox) - E_{1/2}(red)$ is the difference between the half-wave potentials for the oxidation and reduction processes.

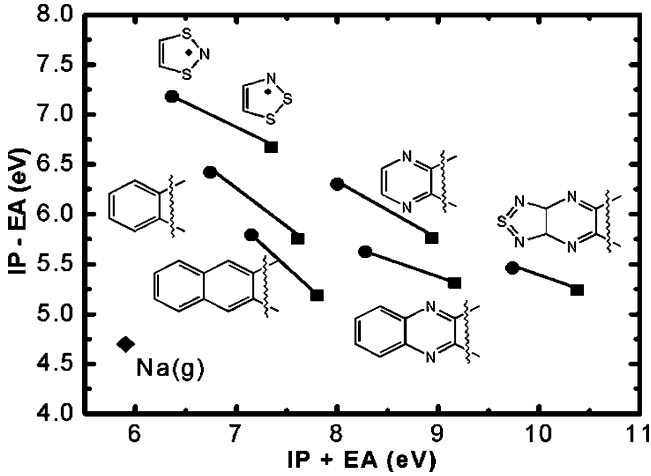
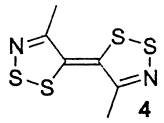


FIGURE 2 Plot of computed (B3LYP/6-31G**) $IP + EA$ vs $IP - EA$ values (in eV) for a series of 1,3,2-DTA (●) and 1,2,3-DTA (■) radicals. The experimental value for Na(g) (♦) is also shown.

The effects are illustrated in Figure 2, which summarizes the computed (B3LYP/6-31G**) *IP* and *EA* values for a series of 1,3,2- and 1,2,3-DTA radicals. The results are presented as a plot of $IP + EA$, i.e., the molecular disproportionation energy ΔH_{disp} or twice the molecular hardness η,[17] against $IP - EA$, or twice the molecular electronegativity χ. We associate atomic metals with elements that are both soft and electronegative, and it is not unreasonable to seek similar features in molecular based conductors. It is apparent from the data presented in Figure 2 that the prototypal DTA radicals **2** and **3** ($R_{4,5} = H$) have quite high disproportionation energies, a simple consequence of the fact that the spin distribution is restricted to a single ring. Moreover, in the case of 1,3,2-radicals, spin density is heavily localized on nitrogen. In the case of the 1,2,3-systems spin density is almost equally partitioned between the nitrogen and the 5-carbon, a feature which provides both problems and opportunities. For example, attempts to isolate, or even observe, the dichloro radical **3** ($R_{4,5} = Cl$) lead to rapid and irreversible C—C bond formation and the formation of a fulvalene derivative **4**.[18] However, as a result of the greater spin density at carbon, 1,2,3-DTA radicals are more responsive to substituent effects. Thus, comparison of the two thiadiazolopyrazino derivatives **5**[19] and **6**,[20] reveals that spin delocalization is enhanced, and the value of ΔH_{disp} reduced in the latter. Interestingly, carbocyclic groups, as in the naphthalene derivative **7**, appear to be equally effective in lowering ΔH_{disp}, but the

resultant systems are less electronegative.[21] From a chemical perspective this translates into radicals that are more sensitive to oxidation, and stronger reducing conditions, both chemical and electrochemical, are required to generate the radicals from the corresponding cations. However, the lowest ΔH_{disp}, for any of the materials illustrated in Figure 2 is still in excess of 5.0 eV, a value substantially greater than that observed experimentally (4.60 eV) for sodium.[22*] But it is apparent, nonetheless, that the ion energetics (*IP* and *EA* values) of dithiazolyl radicals, particularly the 1,2,3-variants, can be improved by judicious choice of substituents.



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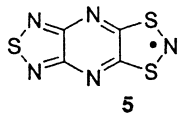

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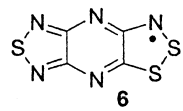

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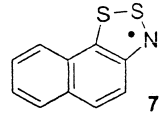
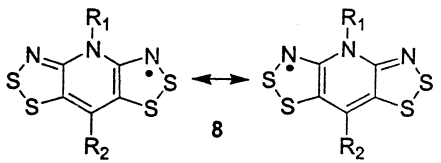


7

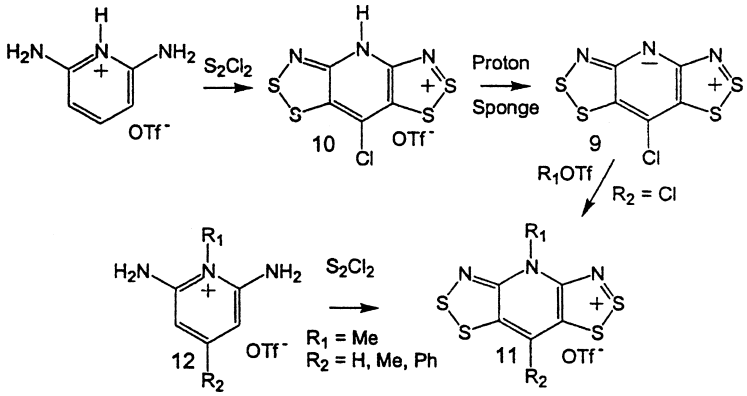
Resonance Stabilized *bis*-Dithiazolyls

While providing encouraging results, i.e., lower disproportionation enthalpies and hence a lower U, electron delocalization in compounds such as **5**–**7** arises from a substituent effect—the attachment of an electron withdrawing group to an otherwise localized DTA radical (**2** or **3**). There are limits to this approach, e.g., is it useful, or even possible, to build more effective electron withdrawing substituents? As an alternative design strategy we are now exploring radicals in which the extent of spin delocalization is enhanced by a resonance interaction between two DTA rings, one a 1,2,3-dithiazolyl radical and the other a closed shell 1,2,3-dithiazole, as in the pyridine bridged compound **8**. In these *bis*(DTA) systems, spin density is shared equally by the two DTA rings, and as a result the molecular ion energetics are much improved over previously studied monofunctional systems. Thus, for $R_1 = R_2 = H$, the computed *IP* and *EA* values are 6.30 and 1.60 eV, respectively, and $\Delta H_{\text{disp}} = 4.7$ eV, a value remarkably similar to that of atomic sodium.



8

*For sodium $\Delta H_{\text{disp}} = IP - EA = 5.14 - 0.55 = 4.59$ eV.



SCHEME 1

A synthetic inroad to this class of compounds was developed by chance, at a time when we were investigating the properties of the Zwitterionic *bis*-dithiazoles **9**.[23] The latter (with $R_2 = Cl$) can be easily prepared, in its protonated form **10**, by a double Herz cyclocondensation of 2,6-diaminopyridinium triflate with sulfur monochloride (Scheme 1).[24] Treatment of **10** with Proton Sponge then liberates the desired Zwitterion, which can be alkylated by an alkyl triflate R_1OTf (R_1 = Me, Et, Pr) to afford a series of quaternary salts **11**. The latter can also be reached more directly starting from the N-alkyl pyridinium salts **12**.[25] Chlorination of the pyridine ring, can be prevented by carrying out the cyclo-condensation reaction at room temperature in the presence of an auxiliary base, i.e., triethylamine.[26] Moreover, when 4-substituted pyridinium salts (R_2 = Ph, Me) are used, suitably modified salts **11** can be generated.[27]

We have explored the redox chemistry of **11** using cyclic voltammetry. Typically three electron transfer processes are observed, corresponding to the −1/0, 0/+1 and +1/+2 couples, as illustrated for **11** (R_1 = Me, R_2 = Cl) in Figure 3. The two more anodic processes are reversible, regardless of the nature of R_2, but the reversibility of the −1/0 wave is dependent on the nature of R_2. Thus, relatively electron withdrawing groups, e.g., R_2 =Cl, Ph, afford a reversible wave, while more electropositive substituents, e.g., R_2 = H, Me, lead to irreversible reduction which we attribute to cleavage of the S–S[28] (or S–N)[29] bonds. The data provide numerical information on two crucial issues. First, the difference between the $E_{1/2}$ values for −1/0 and 0/+1 waves is the cell potential E_{cell}, and for all derivatives studied thus far this is in the order of 0.80–0.85 V, and as such is the lowest observed for any heterocyclic radical. Second, the value of $E_{1/2}$ (0/+1) provides a clear indication of the kind

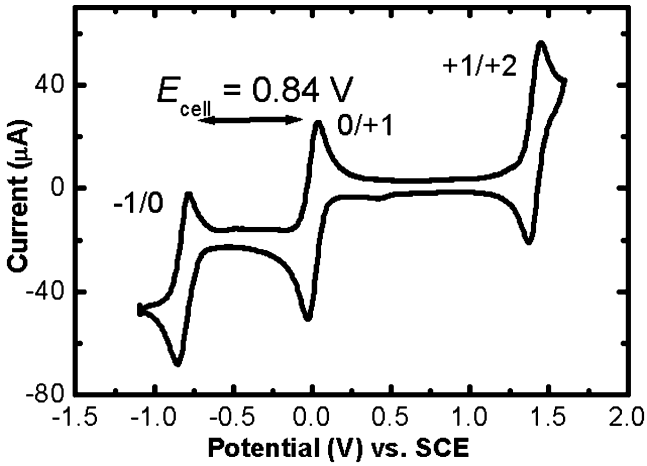


FIGURE 3 CV scan of [**11**][SbF_6] (R_1 = Me, R_2 = Cl) in CH_3CN, [*n*-Bu_4N][PF_6] supporting electrolyte.

of reducing agent that must be used to convert the cation **11** into the desired radical **8**.

We have spent considerable time in the search for single electron transfer (SET) reducing agents with the right potential to reduce these (and/or other) cations to their respective radicals. Table I provides a summary of the reagents that we have found to be useful.

We have structurally characterized a number of *bis*(DTA) derivatives **8**. In all cases the radicals adopt undimerized slipped π-stack structures exhibiting a complex network of close interannular S---S contacts; examples (R_2 = H, Cl; R_1 = Me, Et) are shown in Figure 4. In most cases, ring slippage is lateral, i.e., along the long axis to the molecule, although in ClBPEt, the rings slip longitudinally. The degree of slippage

TABLE I Half-Wave Potentials (in CH_3CN, *n*-Bu_4NPF6, vs SCE) for SET Reducing Agents

Reagent	$E_{1/2}$
Ferrocene[31]	+0.38
Decamethylferrocene[32]	−0.13
$(COOMe)_2$-cobaltocene[33]	−0.41
TDAE[34]	−0.61, −0.78
	−0.62 (2e-, DMF)
Cobaltocene[35]	−0.93

TDAE = tetrakis(dimethylamino)ethylene

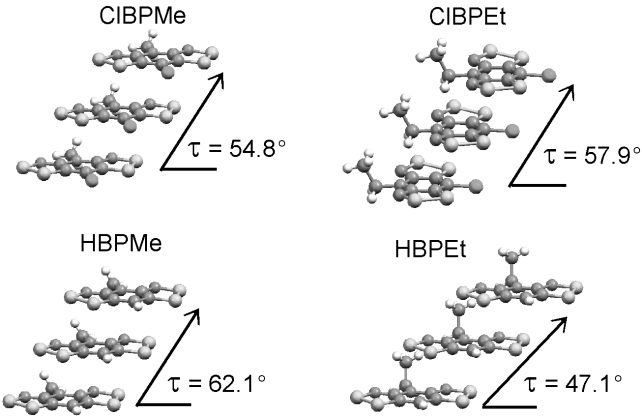


FIGURE 4 Slipped π-stacks structures in **8** (R_2 = H, Cl; R_1 = Me, Et).

is conveniently defined in terms of τ, the angle made between the mean plane of the heterocyclic skeleton and the stacking axis. Values of τ are provided in Figure 4. In the case of ClBPMe a phase change has been observed below 93K to an even more sharply slipped π-stack structure.

Magnetic susceptibility measurements on the above compounds reveal essentially paramagnetic behaviour at room temperature, with minor deviations at lower temperatures arising from weak ferro- or anti-ferromagnetic interactions. Variable temperature single crystal conductivity measurements suggest semiconductive rather than metallic behavior, with room temperature conductivities σ_{RT} in the range 10^{-5}–10^{-6} S cm^{-1} and thermal activation energies E_a = 0.40–0.48 eV. In order to place these results in context, we have performed Extended Hückel band structure calculations, the results of which, presented in the form of dispersion curves for the crystal orbitals arising from the four SOMOs in the unit cells, are plotted in Figure 5.

As can be seen, the computed bandwidths are in the order of 0.4–0.5 eV, values which compare well with those seen in organic CT superconductors, but not as large as we had hoped for, given the apparent tightness of the crystal structures and the number and closeness of the S---S contacts. Surprisingly, the greatest dispersion is found for HBPEt, for which lateral slippage is largest (τ is a minimum). In order to rationalize these findings we carried out a series of calculations on model π-stacks with different slippage angles τ. The results reveal that while very large bandwidths—over 2 eV—can be attained with superimposed π-stacking, it is markedly reduced as a result of slippage. Extreme slippage, leading to values of τ less than 45°, can, however, improve intermolecular overlap significantly and hence afford broader

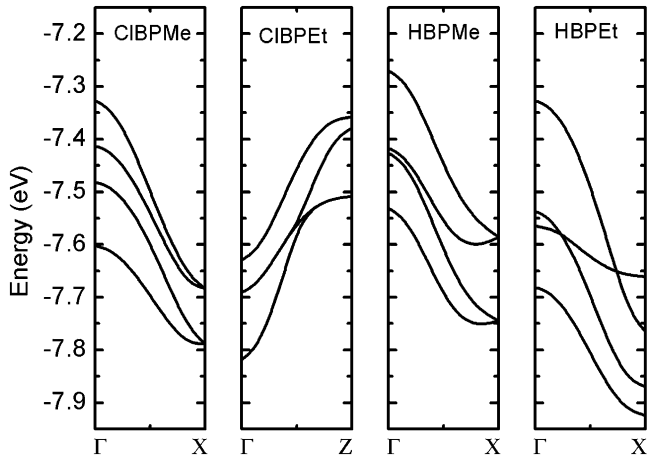


FIGURE 5 Crystal orbital dispersion in **8** (R_2 = H, Cl; R_1 = Me, Et).

bands. This, we believe, is the origin of the slightly higher conductivity observed for HBPEt.

There remains a quandary. The Extended Hückel band calculations ignore electron correlation, and as a result predict that the *bis*(DTA) radicals should possess a half-filled energy band and exhibit metallic ground states, but the transport property measurements indicate otherwise. The materials exhibit Curie paramagnetism (not Pauli paramagnetism) at room temperature, and their conductivity is activated. In

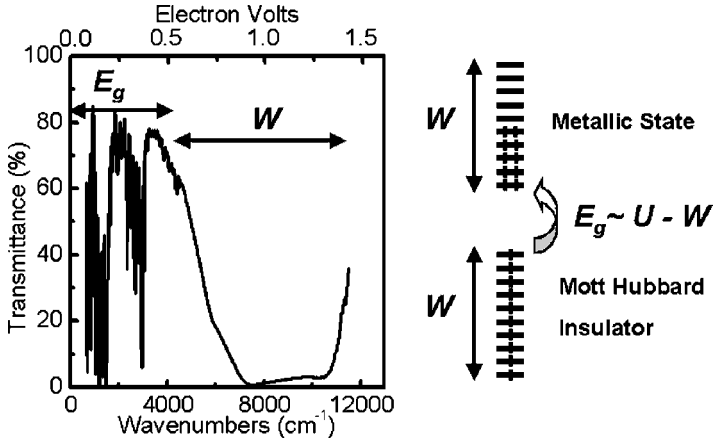
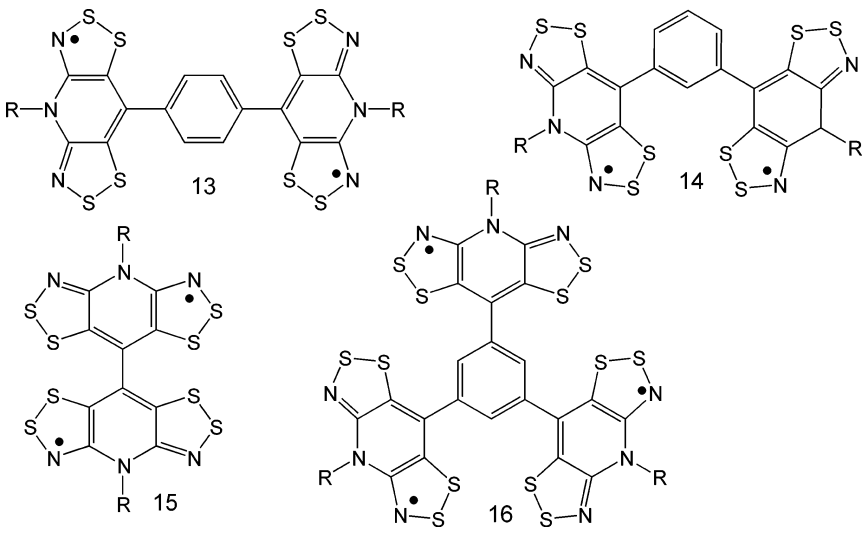


FIGURE 6 Optical spectrum (left) and electronic structure (right) of **8** (R_2 = H, R_1 = Et).

order to clarify the electronic structure of these radicals we have measured the solid state optical transmission spectrum of **8** (R_2 = H, R_1 = Et). It reveals a well-developed conduction band of bandwidth W separated from an insulating ground state by an energy gap E_g (Figure 6). These features point to a Mott-Hubbard insulator ground state in which each of the levels in the energy bands shown in Figure 5 is half-filled (Figure 6).[35] The conductive state, in which half of the levels in the band are doubly occupied, lies above the localized valence state. Thus, while overlap and consequent spreading of the conduction band partially offsets the effects of electron correlation, there remains a *residual* onsite Coulomb repulsion ($E_g \sim U - W$) which leads to activated conductivity.

SUMMARY

The development of NRC materials faces several design challenges. The key structural problem is a Peierls instability—the tendency of the radicals to dimerize—which in the case of the *bis*(DTA) radicals described here has been effectively suppressed by the beltline R_1 and R_2 substituents. The electronic problem, the *complete* suppression of the onsite Coulomb repulsion energy U, remains. Overcoming this hurdle will require the design of even softer radicals and/or systems with larger electronic bandwidths W. In the future we look to the development of selenium containing variants of **8**, and the elaboration of polyfunctional assemblies such as **13–16** where, as in polyfunctional dithiadiazolyls,[8c,d] more tightly knit structures and larger bandwidths are to be expected.



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