Potential Linear-Chain Organic Ferromagnets

Kazunari Yoshizawa and Roald Hoffmann*

Abstract: The electronic structures of conjugated polymers containing methyl radicals, carbenes, and nitrogen-based radicals coupled in various ways through benzene rings are examined, employing band-structure calculations in the extended Hückel approximation. The structural and electronic properties of polymers with a *para*-phenylene or *meta*-phenylene coupling unit are compared. In the polymer with methyl radicals coupled through a *para*-phenylene unit, a pairing or Peierls distortion occurs to remove the degeneracy at the Fermi level. The resulting bandgap is nevertheless relatively small; we conclude that such polymers are likely to exhibit high electrical conductivity upon doping, very much like polyacetylene. On the other hand, in the polymers with a *meta*-phenylene coupling unit, striking symmetry-determined, half-occupied narrow bands appear at the Fermi level and contribute to the stability of the ferromagnetic state. The relation of a potential ferromagnetic state to metallic, CDW, and SDW states is discussed from the viewpoint of orbital interactions in extended systems. We suggest novel 3- and 4-fold helical structures for the *meta*-phenylene-coupled polymers.

Keywords: conjugation · ferromagnetism · helices · magnetic properties · polymers

Introduction

Conjugated polymers may be semiconducting, metallic, superconducting, or photoconducting—the gamut of electronic properties.[1] The archetypical such polymer, polyene, now called polyacetylene, has been most extensively investigated, both theoretically and experimentally. But many other kinds of conjugated polymers with intriguing electronic properties have been developed since the characterization of polyacetylene films.[2]

The design of high-spin or ferromagnetic materials based on molecular systems is a challenge for our times.[3-8] Potentially, conjugated polymers could also serve as ferromagnetic materials. Magnetic interactions through a *meta*-phenylene coupling unit have figured importantly in the design of molecular ferromagnets.[9-18] In this strategy, a phenyl ring plays a significant role both in the ferromagnetic coupling and in the stabilization of radicals, as suggested by Mataga.[19] The same coupling entities enter our considerations.

Recently yet another strategy has been employed for several types of molecular ferromagnets, one based on intermolecular magnetic coupling in three-dimensional molecular crystals.[20-24] As is well known, one-dimensional systems can show bulk ferromagnetic properties only at 0 K.[25] However, since in real crystals there are almost always three-dimensional interactions, ferromagnetic or antiferromagnetic ordering may appear even in seemingly one-dimensional organic polymers at a finite temperature.

There is a large amount of theoretical work on biradicals[26-35] and some on triradicals[36] coupled through a *meta*-phenylene unit, using molecular orbital (MO) and valence bond (VB) methods. However, studies on infinite systems of linear-chain organic ferromagnets are relatively rare. Several calculations have been carried out at the Hückel, Hubbard, and semiempirical unrestricted Hartree–Fock (UHF) levels of approximation by Tyutyulkov et al.,[37] Nasu,[38] and Yamabe et al.[39] In particular, Tyutyulkov and co-workers have discussed extensively many possible kinds of linear-chain organic ferromagnets. Each of the computational methods applied has its merits and demerits; the Hückel method is clearly oversimplified, and the SCF methods have a tendency to overestimate band gaps, although they include critical electron–electron interactions in a semiempirical manner. Descriptions of the density of states (DOS), which provide us with valuable information about the electronic structure of potentially ferromagnetic polymers, were by and large not given in these studies, except in refs. [39a–b].

In this article we study the structural and electronic properties of conjugated polymers containing several kinds of radicals coupled through a *para*-phenylene or *meta*-phenylene unit. The method we use is the extended Hückel theory.[40] Our calculations as well as those of others[37-39] are certainly based on simplified models, as mentioned above. We explain, from the viewpoint of orbital interactions in extended systems, why ferromagnetic interactions appear among radicals through a *meta*-phenylene coupler, in contrast to their absence for a *para*-phenylene coupler. Although the extended Hückel theory neglects explicit electron–electron repulsions, the method includes overlap of all valence atomic orbitals and has been relatively successful in describing the bonding of conjugated polymers and transition metals with various linear-chain structures.[41] We discuss the electronic and magnetic structures of

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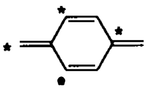
linear-chain organic ferromagnets, supplementing the extended Hückel calculations by an estimate of the electron interaction parameters that determine the actual ordering of various possible states of the polymer.

Another important phenomenon relevant to this paper is the potential instability of a metallic state, which results from a partially occupied band in one-dimensional electronic systems.[42–46] This phenomenon is known as a Peierls or off-diagonal charge-density wave (CDW) transition. Still another important broken symmetry state in one-dimensional systems is a spin-density wave (SDW) state, where the SDW usually represents an antiferromagnetic spin array. The ferromagnetic state of one-dimensional systems competes with the metallic, CDW, and SDW states. We compare the relative stabilities of these electronic states in the context of a chemical viewpoint of extended systems, which we hope clarifies the context in which these states compete to be the ground state.[37–39] We treat the methyl radical ($HC^{\cdot}$), methylene ($C^{\cdot\cdot}$), aminyl ($N^{\cdot}$), aminium ($HN^{\cdot+}$), and nitroxide ($NO^{\cdot}$) as spin carriers accommodated in the linear-chain structures mentioned above.

The main purpose of this paper is to show how ferromagnetic interactions occur among radicals through a *meta*-phenylene coupler and how they are different from the related *para*-phenylene cases, in spite of their structural similarities. There are several band calculations of *meta*-phenylene-coupled polymers, and explanations for the origin of the ferromagnetic interactions are available in the literature.[37–39] A reviewer has remarked that there is a tutorial character to this paper; this is certainly true.

Results and Discussion

Some Preliminary Considerations: Before describing the band structures of the title polymers, it is wise to look at the electronic structures of *para*-quinodimethane **1** and *meta*-quinodimethane **2**. Since a pivotal Longuet-Higgins' prediction,[26] much work has been concerned with these important Kekulé and non-Kekulé structures. Compounds **1** and **2** have zero and two π nonbonding MOs (NBMOs), respectively. This follows from a useful general relation that the number of π NBMOs is equal to $N - 2T$, where N is the number of carbons and T is the maximum number of double bonds occurring in any resonance structure. Compounds **1** and **2** are predicted to be a ground-state singlet and triplet, respectively, by Hund's rule.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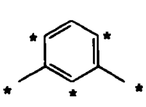
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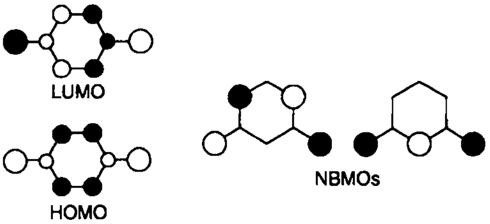
The frontier orbitals of **1** and **2** are shown schematically in Scheme 1. The reason that **2** is a ground-state triplet derives from the *nondisjoint* character of the π NBMOs of this molecule. As explained by Borden and Davidson,[47] when π NBMOs are nondisjoint, that is, while orthogonal they are very much coextensive in space, a ground-state triplet can be expected. This is because exchange interactions are large in such a case.



Scheme 1.

In some other systems, the π NBMOs *can be chosen* in such a way that they are *disjoint*, that is, they do not share any atoms.[47] For such molecules, singlet and triplet states are degenerate to a first approximation, since the exchange interactions are small. The best example of a molecule with disjoint π NBMOs is probably that of square cyclobutadiene;[44,47] another is biallyl or tetramethyleneethane.

Another approach to the prediction of a ground spin-state is based on the VB method. Molecules **1** and **2** are alternant hydrocarbons—the conjugated atoms may be alternately labeled as "starred" and "unstarred", such that no two atoms of the same label are directly linked. According to Ovchinnikov,[48] the total spin quantum number S is equal to $|N^*-N|/2$, where N^* and N are the numbers of starred and unstarred atoms, respectively. The basis of this rule is clear: assuming that spins on adjacent atoms are antiparallel, that is, the exchange integral $J<0$, the lowest energy is expected when all the starred atoms have spin $^1/_2$ (up spin) and all the unstarred atoms have spin $-^1/_2$ (down spin). In the present context **1** and **2** are predicted to have $S = 0$ and 1, respectively. This result is consistent with the prediction based on Longuet-Higgins' relation described above, although several well-understood exceptions are currently known.[47c]

Although we have not mentioned *para*-quinodimethane **1**, its electronic structure is also very interesting from the viewpoint of orbital interaction. The HOMO of **1** is composed of a bonding combination of the benzene e_{2u} *LUMO* and the π orbitals of two methylenes; the LUMO of **1** is composed of an antibonding combination of the benzene e_{1g} *HOMO* and two methylene π orbitals, as shown above in Scheme 1. The HOMO–LUMO gap of **1** is consequently very small, 0.62β, within the framework of the Hückel method (benzene has a gap of 2β), and as a result **1** is highly reactive. It polymerizes readily in condensed phases. Historically interesting discussions of the reactivity of **1**, by Coulson et al. and by Szwarc, may be found in ref. [49].

In an earlier paper we derived a simple expression for the effective exchange interaction J in the context of a Heisenberg Hamiltonian.[50] J, given by Equation (1), is governed in molecular systems mainly by the orbital overlap S_{ab} as well as the exchange integral.

$$J = 5(h_{aa} + h_{bb})S_{ab}^2 - 2(aa|bb)S_{ab}^2 + 2(ab|ba) \qquad (1)$$

where

$$h_{aa} = \int a^*(1)h(1)a(1)d\tau(1)$$

and $(aa|bb)$ and $(ab|ba)$ are, respectively, the Coulomb integral and exchange integral, described below, in terms of interacting SOMOs (singly occupied MOs) a and b.

$$(aa|bb) = \iint a^*(1)a(1)\frac{1}{r_{12}}b^*(2)b(2)d\tau(1)d\tau(2)$$

$$(ab|ba) = \iint a^*(1)b(1)\frac{1}{r_{12}}b^*(2)a(2)d\tau(1)d\tau(2)$$

The first consequence of Equation (1) is that a triplet state is stabilized when the overlap is small. Second, to achieve the situation of a triplet well below a singlet, it is essential that interacting SOMOs should be noded, and geometrically arranged in very specific ways. That is, interacting SOMOs must be highly overlapped to maximize the exchange interactions, although their net overlap must cancel.[50] In this context, the π NBMOs of **2**, indicated in Scheme 1, are quite appropriate for the appearance of ferromagnetic coupling.

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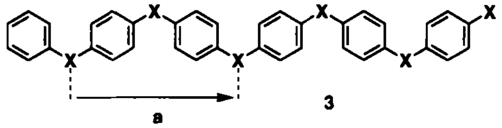
The Polymers Considered: Having described briefly the electronic structures of molecules **1** and **2**, let us now construct conjugated polymers from both molecules. Consider polymers **3** and **4**, which have radicals ($X = HC^{\cdot}$, $C^{\cdot\cdot}$, $N^{\cdot}$, $HN^{\cdot +}$, and $NO^{\cdot}$) coupled through *para*-phenylene and *meta*-phenylene units, respectively.



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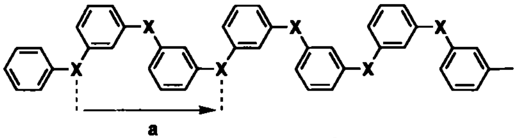

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In discussing the structure of these polymers we immediately confront a special problem. In the planar geometries shown, there are clearly steric problems for the *ortho*-hydrogens of neighboring rings. These may be alleviated in two ways: by an increase in the C-X-C angle, or by rotation of the benzene rings out of the C-X-C plane; or indeed by both. Previous studies of *meta*-phenylene chains **4** based on the π electron approximation[37, 38] have not faced up to this steric problem. In previous UHF calculations including all valence electrons,[39a, b, e] the *ortho*-hydrogen contact has been alleviated by opening the C-X-C angles to 140°.

The C-X-C angle increase (say up to 150°) is actually a matter of preference for the methylenes; triplet methylene (CH_2) has an open H-C-H angle of 134°,[51] and diphenylcarbene has an angle of about 140–150°.[52] For the methyl, aminium, and nitroxide radicals one might have thought that a C-X-C angle of between 120° and 130° would be favored. The actual C-X-C angles of **3** and **4** are determined by a balance between the steric problems caused by the *ortho*-hydrogens' close contacts and the π conjugation between the radical site and neighboring benzene rings.

Even if the C-X-C angle were opened to 140° while retaining a planar geometry, the distance between the *ortho*-hydrogens, about 1.5 Å, is still too small. We think these molecules must be nonplanar. The other way to solve the steric problem, rotation of the benzene rings, is no problem for the *para*-phenylene case (various modes are possible). However, for the *meta*-phenylene chain **4**, we encounter a real difficulty—any rotation around X–C leads to nonlinear polymers *and*, despite much effort, previous studies[39a, b, e] have found no translationally or helically periodic structures.

Since the analysis is simpler for the all-planar polymers, we first study these (with C-X-C angle 140°). Then we also look at nonplanar geometries, optimized with the extended Hückel method.[40] We will examine in some detail several novel 3-fold and 4-fold helical structures we have discovered for the *meta*-phenylene chain. Other geometrical parameters and the method of calculation are given below.

The *para*-Phenylenemethylene Bridged Polymers: Although our main concern in this paper lies in the magnetic properties of linear-chain polymers, this *para*-phenylene bridged polymer is a recent synthetic target in the field of conducting polymers. The interesting electronic properties of this polymer were calculated ten years ago by Boudreaux et al.[53] The possible Peierls distortion of the planar form of this polymer was recently discussed by Kertesz.[54] Although many attempts to prepare similar types of polymers with a small bandgap have been made recently,[55, 56] to the best of our knowledge the polymer under discussion has not yet been synthesized.

Let us consider first the structural and electronic properties of **3** ($X = HC^{\cdot}$) with *para*-phenylene coupling units. We assume equal C–C bond lengths of 1.42 Å around the bridge C–H. Figure 1 shows the band structure and density of states (DOS) curve of **3** ($X = HC^{\cdot}$). The shaded area of the DOS is the contribution from π bands; the dotted line marks the Fermi level.

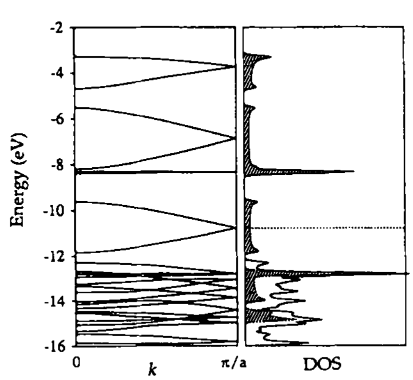
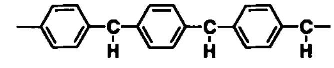


Fig. 1. Band structure and DOS (density of states) of planar poly(*para*-phenylenemethine) with "benzenoid" rings and equal C–C bond lengths in the bridge moieties, indicated in **3**. The C-X-C angle is 140°. The shaded area of the DOS shows the contribution from π bands, and the dotted line marks the Fermi level.

The orbitals of **3** are not very complicated, but we really want to understand them in some detail. For that purpose, it is instructive to consider first the "linear" polymer **5**. The perturbation of turning **3** into **5** (or vice versa) is severe in the σ system, but the effect on the π system of the molecule, which is critical to us, should be small. The advantage of **5** is that its unit cell is half of that of **3**.



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The band structure and DOS of **5** are shown in Figure 2. Note how similar the DOS of **3** (Fig. 1) is to that of **5** (Fig. 2), and yet how much simpler the band structure of **5** appears. There is a strict σ–π separation in the polymer; the contribution of the π bands in the DOS is marked by the shaded area. Critical to our further discussion is the π band crossed by the Fermi level. Representative orbitals in this band, at $k = 0$ and π/a, are shown in Scheme 2. Note that these orbitals arise simply from symmetry-conditioned interactions of the bridging Cπ-radical lobes with the antibonding benzene e_{2u} components at $k = 0$, and with the bonding benzene e_{1g} at $k = \pi/a$. This interaction gives rise to the upward slope of this band as one passes through the Brillouin zone.

Let us now return to the more realistic "kinked" *para*-phenylenemethylene polymer, **3**. The motion from **5** to **3** involves a bending at $X = HC^{\cdot}$, and a consequent doubling of the unit cell. All the bands are "folded back",[44] a direct consequence of the 2_1 screw axis. This gives rise to the degeneracy at $k = \pi/a$ noted in Figure 1.

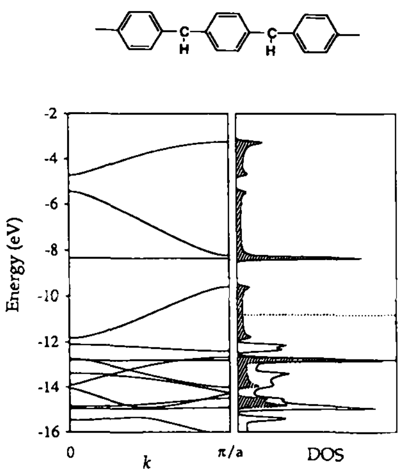
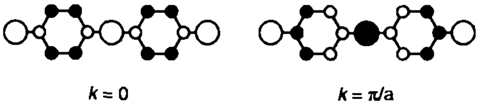


Fig. 2. Band structure and DOS of hypothetical "linear" poly(*para*-phenylenemethine) **5**. The dotted line marks the Fermi level; the shaded area is the contribution of the π bands to the total DOS.



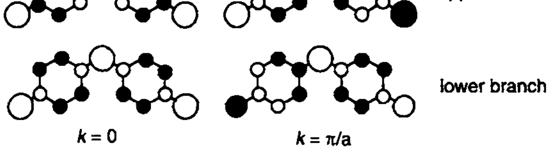
Scheme 2.

An interesting feature of the band structures of Figures 1 and 2 is the presence of very narrow π bands around −13 and −8 eV. These are descended from the benzene e_{1g} HOMO and e_{2u} LUMO, respectively. Since one component of these degenerate pairs has zero coefficient at the *para* sites of benzene, there is no nearest neighbor overlap between neighboring unit cells, and as a result the dispersion of these two bands is small.[41b] These characteristic narrow bands have little effect on the structural and electronic properties of this polymer, because they are far away from the Fermi level. We mention them here because analogous narrow bands, right at the Fermi level, will be of critical significance in the *meta*-phenylene-coupled case.

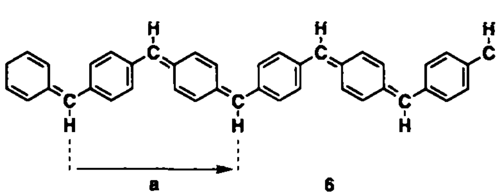
The Fermi level for **3** comes precisely at the contact of two π bands, at $k = \pi/a$. This is a typical feature of one-dimensional electronic systems with 2_1 symmetry, such as polyacetylene.[41b, g, 44] A Peierls or off-diagonal CDW distortion is consequently expected to occur in this polymer, namely, a coupling of electron and phonon modes, in particular a "pairing distortion" for such a half-occupied band.[44]

The orbitals at $k = 0$ and π/a of the metallic band are shown in Scheme 3 on the right. Note that the orbitals at $k = 0$ are just those we derived for the "halved-unit-cell" polymer **5**.

The critical orbitals now become those at $k = \pi/a$. With some work it is possible to derive these also from those of the more symmetrical polymer **5**, but let us for the moment accept that they are as shown in Scheme 3. From the shape of these orbitals at $k = \pi/a$, we are led to a specific distorted structure, that shown in **6**, a structure with alternating "benzenoid" and "quinonoid" rings. Note that in **6** the bonding character of the lower branch at $k = \pi/a$ (Scheme 3, right bottom) will be strengthened and its antibonding character will be weakened. This deformation will then open a substantial gap at the Fermi level. A similar deformation was suggested for the pernigraniline form of polyaniline.[57, 58] There are some useful calculations concerning the geometries and electronic properties of various forms of polyaniline.[58]



Scheme 3.



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Our theoretical method is not reliable for distance optimization, so we tentatively assume an alternation of C–C bond lengths in the bridge moieties of 1.46 Å and 1.38 Å. The difference of these bond lengths is 0.08 Å, corresponding to that observed in *trans*-polyacetylene.[59] We take the geometrical parameters of the quinonoid rings in **6** from those of *para*-benzoquinone (see Methods of Calculation). The resulting band structure is shown in Figure 3. As expected, the degeneracies of all bands at $k = \pi/a$ are removed. The lower branch of the metallic band is shifted down in comparison with that of the regular structure **3** (X = HC˙), while the upper branch is shifted up. The opening of energy gap at the Fermi level leads to a stabilization of the alternating structure.

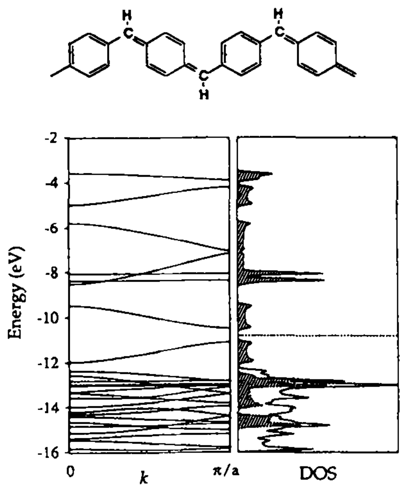


Fig. 3. Band structure and DOS of poly(*para*-phenylenemethine) with alternating "benzenoid" and "quinonoid" rings, indicated in **6**. The degeneracy of the bands at the Fermi level seen in Figure 1 is removed, owing to the pairing distortion.

Let us now examine a more realistic *nonplanar* polymer geometry. Since the C-X-C bridging angle (θ) and the benzenoid ring out-of-plane torsion (τ) are highly correlated, we examined the total energy as a function of these two angles in detail. θ and τ were optimized at 130 and 54°, respectively. The other geometrical parameters were fixed as those of the alternating "benzenoid–quinonoid" ring structure discussed above. Figure 4 shows the band structure and DOS of nonplanar bond-alternating **6** (X = HC˙). We can no longer separate clearly π and σ orbitals in the nonplanar geometry. However, the bands and

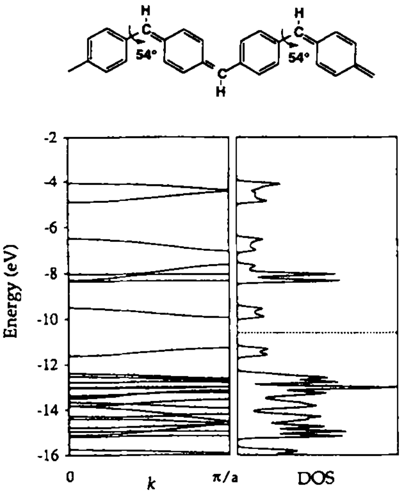


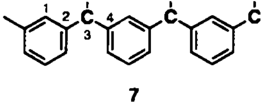
Fig. 4. Band structure and DOS of nonplanar poly(*para*-phenylenemethine) with alternating "benzenoid" and "quinonoid" rings. The benzenoid rings are twisted 54° out of the polymer plane, and the C-X-C angle is 130°. The bandgap is 1.33 eV.

DOS curve are quite similar to those of Figure 3. The dispersion of the bands in the nonplanar polymer is a little smaller and the bandgap is twice as large as that in the planar structure.

Interestingly, the bandgap of this polymer is in the end relatively small (1.33 eV), in spite of its nonplanar geometry. This small bandgap is consistent with a previous calculation using the valence-effective-Hamiltonian method.[53] This is probably a direct consequence of the small HOMO–LUMO gap of *para*-quinodimethane **1** (0.62β) in the Hückel approximation, as mentioned above. This result contrasts with the case of poly(*para*-phenylene).[41b] The HOMO–LUMO gap of benzene is 2β and the bandgap of planar poly(*para*-phenylene) with benzenoid rings is 1.89 eV; the correlation between HOMO–LUMO gap and bandgap is clearly seen. We anticipate that polymer **3** (**6**) should exhibit high electrical conductivity on doping.

The *meta*-Phenylenemethylene Bridged Polymer: Let us next look at the band structure and DOS of some polymers with a *meta*-phenylene coupling unit. Experimentally, high-spin states up to $S = 5$ (10 radicals) of the oligomers of this structure (geometry unknown) have been characterized by Rajca et al.[18] The possibility of much higher-spin states has been discussed.

Planar polymer **4** is actually not the simplest way (within the admittedly artificial planar constraint) of *meta*-coupling radicals through benzene rings. Polymer **7** is another realization; it has only one benzene ring and one methyl radical per unit cell. The factor mitigating against any geometry close to **7** is, of course, that each benzene ring in **7** is involved in two troublesome steric contacts with the neighboring *ortho*-hydrogens. At first sight it seems that polymers **4** and **7** have similar steric problems; two hydrogens in each phenyl ring are in steric difficulty. However, **7** has, we think, a greater steric problem. To retain a linear geometry in **7** it is necessary to perturb not only the angle at the bridging group (the C_2-C_3-C_4 angle) but also to change another angle (we took, for instance, the C_1-C_2-C_3 and C_2-C_3-C_4 angles to be 130 and 140°, respectively).



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Putting aside the steric problem for the moment, while not forgetting it, we carried out a calculation on **7**. Its band structure and DOS are shown in Figure 5. The shaded area of the first DOS (center) is the contribution from all π bands, and that of the second DOS (right) is the contribution from π orbitals at the radical centers. Note the single nonbonding band at the Fermi level. Its make-up at $k = 0$ is indicated in Scheme 4 left, at $k = \pi/a$ in Scheme 4 right. These levels look familiar, don't they? They are the π NBMOs of *meta*-quinodimethane. It is immediately clear why this band is so narrow; there is zero nearest neighbor overlap at the cell junction.

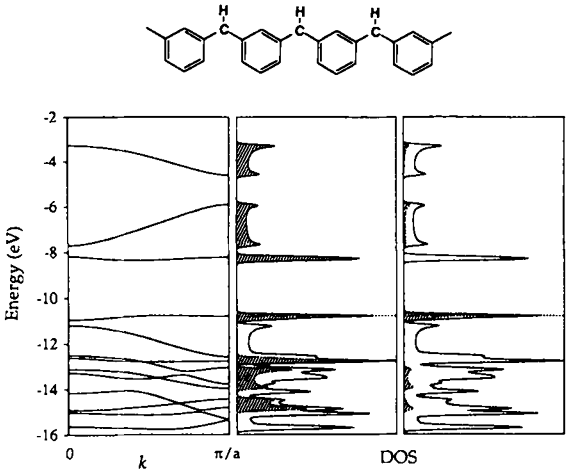
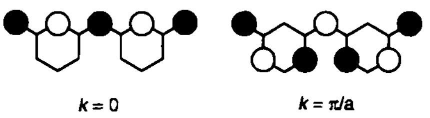


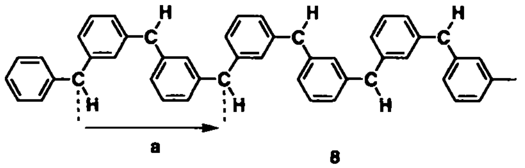
Fig. 5. Band structure and DOS of a simple planar (and sterically uncomfortable) poly(*meta*-phenylenemethine) **7**. The shaded area of the first DOS (center) is the contribution from π bands, and that of the second DOS (right) is the contribution just from the π orbitals at the radical centers.



Scheme 4.

Otherwise, the band structure of **7** is quite similar to that of the *para*-phenylene-coupled polymer, **5**. The two narrow bands previously noted at −13 and −8 eV also appear in the *meta*-phenylene-coupled polymer. The origin of these two narrow bands is same as that of the corresponding bands in **3** (X = HC˙).

We proceed to polymer **4** (X = HC˙), a planar geometry, shown again in **8**. From what we learned from the *para*-phenylene case we expect a clear relation of the electronic structure of this polymer to its simpler analogue **7**. The unit cell is doubled, so there should be twice as many bands, folded back, and a very similar total DOS. In Figure 6 we show the band structure and DOS of **8**. At the Fermi level, we see what seems to be a single band. Actually this is a pair of extremely narrow half-occupied folded-back bands.



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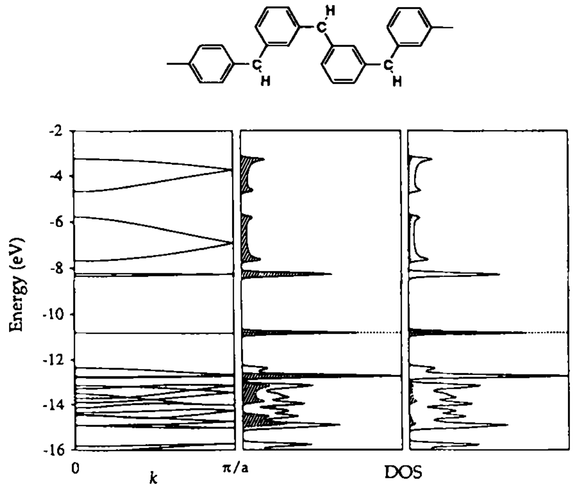
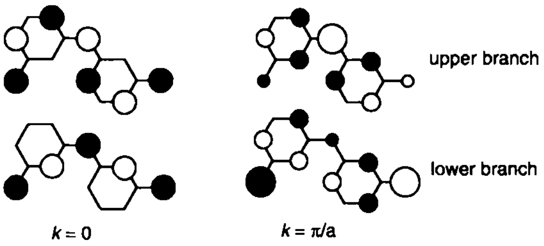


Fig. 6. Band structure and DOS of planar poly(*meta*-phenylenemethine) **4** or **8**. The shaded area of the first DOS (center) is the contribution from π bands, and that of the second DOS (right) is the contribution just from the π orbitals at the radical centers. Note the two narrow bands (half-occupied), appearing as a single band, just at the Fermi level.

The bands at the Fermi level are narrow because the orbitals that make them up (see Scheme 5) are very much like the π NBMOs of *meta*-quinodimethane, shown previously in Scheme 1: these do not have any nearest neighbor overlap at the unit cell junction. At $k = 0$ we see the *meta*-quinodimethane NBMOs clearly; at $k = \pi/a$ the orbitals are mixed.



Scheme 5.

The reader may also note the resemblance of the orbitals at $k = \pi/a$ to the NBMO of a benzyl system. The energy splitting between the two bands at $k = 0$ is only a minute 0.002 eV; all these states are essentially degenerate. The width of the corresponding band at the Fermi level of **3**, the *para*-phenylene-coupled polymer (X = HC˙), is 2.2 eV, as we saw. That is quite a remarkable contrast. A narrow band, as calculated for the *meta*-phenylene-coupled polymer, is appropriate for electron localization and for the appearance of ferromagnetism.

Helical Geometries of Poly(*meta*-phenylenemethylene): It is possible to realize *nonplanar* geometries of *meta*-phenylene-coupled polymers with substantially less steric strain than the cases heretofore considered. Such polymers are perforce helical. Figure 7 shows a lovely periodic 3-fold helical chain we found. The unit cell contains three benzene rings and three methyl radicals. This geometry, not previously suggested in the literature to our knowledge, is the first sterically satisfactory nonplanar geometry for *meta*-phenylene-coupled polymers.

Actually there is a whole family of 3-fold helices, of which the structure shown in Figure 7 is but one example. A given torsion angle fixes a certain "rise" along the helical axis. To be more specific, in this 3-fold helical structure the bridging angle (θ) at the X and the torsion of neighboring benzene rings (τ) are related as shown in Equation (2), in which $\theta > 120°$. By means of ex-

$$\{2\pi-(\theta+120°)\}/\cos\tau = 120° \quad (2)$$

tended Hückel method total energies, θ and τ are optimized at $\theta = 130°$ and $\tau_{1-2-3-4} = \tau_{2-3-4-5} = 23.5°$, respectively, subject to the condition of Equation (2). The net torsion is similar to that of the *para*-phenylene-coupled polymer described above—there one ring "does all the rotating". Since the distance between the *ortho*-hydrogens of neighboring rings is 2.1 Å, steric problems are virtually avoided in the helical structure.

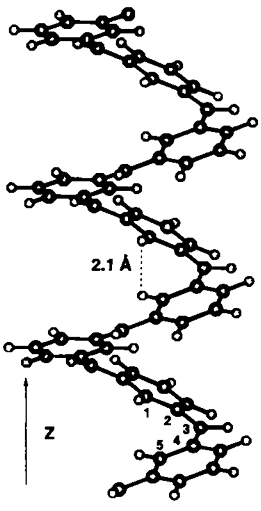


Fig. 7. Threefold helical geometry of a *meta*-phenylene-coupled polymer **4** (HC˙). Dihedral angles, $\tau_{1-2-3-4} = \tau_{2-3-4-5} = 23.5°$.

Out-of-plane torsion, as indicated in **9**, is, of course, characteristic of diphenyl-substituted systems.[60] Our dihedral angle ($\tau_{1-2-3-4} = \tau_{2-3-4-5} = 23.5°$), indicated in Figure 7, is near to the values obtained for diphenylamine (26.2°) and diphenylaminium (25.5°), optimized with the ab initio STO-3G method.[60d]

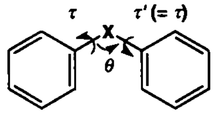


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Figure 8 shows the band structure and DOS of **4** (X = HC˙) with this 3-fold helical structure. All of the bands are folded back both at the zone edge ($k = \pi/a$) and at the zone center ($k = 0$); this is a consequence of the 3_1 screw axis.[44] The DOS profile is quite similar to those of Figures 5 and 6. Once again this is because in this polymer there is little overlap between neighboring cells for certain orbitals, owing to its *meta*-phenylene-coupled structure. Although π and σ orbitals cannot be strictly separated in the nonplanar geometry, the projection in the DOS curve gives the contribution from the p orbital

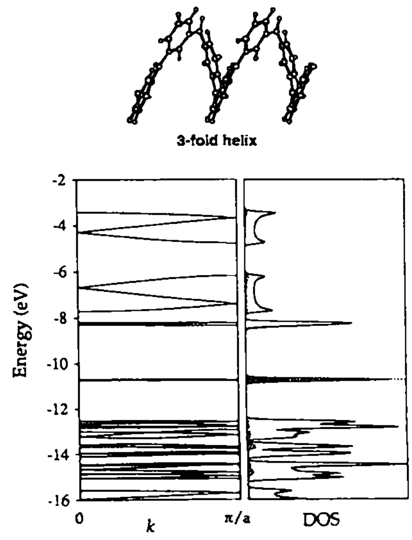


Fig. 8. Band Structure and DOS of poly(*meta*-phenylenemethine) with a 3-fold helical structure. The projection in the DOS signifies the contribution from the pseudo-π orbitals at the radical centers.

perpendicular to the local trigonal plane at the radical centers. Note that the narrow band at the Fermi level is mainly composed of these pseudo-π orbitals.

Magnetic and Other States of the Polymer: Let us consider the relative stabilities of localized and delocalized (nonmagnetic metallic) states of a half-occupied band, that is, what is called the Mott–Hubbard condition.[61] Taking into account the dynamics of electrons in a narrow band, Hubbard derived a criterion for a localized state lying below a metallic state [Eq. (3),

$$W < (2/\sqrt{3})U \tag{3}$$

where W is the bandwidth and U the on-site Coulomb repulsion]. If U is large, electrons tend to localize well within a molecular unit cell, so as to reduce Coulomb interactions. A similar condition, derived by Whangbo[61] in terms of the Hartree–Fock theory, is given by Equation (4). These important rela-

$$W<(\pi/4)U \tag{4}$$

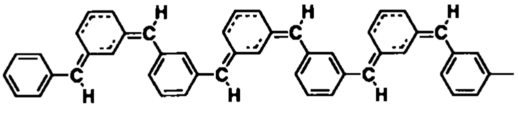
tions provide a criterion for the relative stabilities of localized and metallic states. The localized state in these discussions is the ferromagnetic state.[61]

These relations tell us that electron-localization occurs when the bandwidth approximated by $4|\beta|$ is small. Here β is resonance or transfer integral, and its magnitude is a direct consequence of overlap between neighboring unit cells.[44,45] This discussion is analogous to that of the singlet–triplet separation in molecular systems.[62] U is often approximated by $I_p - E_a$, where I_p and E_a designate ionization potential and electron affinity, respectively. If one looks for a molecule to estimate U for polymer **3** or **4** (X = HC$^\cdot$), styrene seems appropriate. Based on experimental values for styrene ($I_p = 8.42$ eV and $E_a = -0.25$ eV), U is estimated to be 8.67 eV. However, this molecule-based value should be reduced in solids, owing to a polarization effect.[63] Although it is thus difficult to estimate U, the metallic (delocalized) state is unlikely to manifest itself either in **3** or **4** (X = HC$^\cdot$), because their full bandwidths are 2.2 and 0.002 eV, respectively.

We need also to consider the relative stabilities of the ferromagnetic and off-diagonal CDW states of **4** (X = HC$^\cdot$), since this is usually the most important broken-symmetry electronic state of one-dimensional systems. However, it is hard to estimate the intersite repulsion V, necessary to evaluate the relative energies of these states.[61a] Let us discuss, then, on the basis of the orbital patterns of **4** (X = HC$^\cdot$) at the Fermi level, whether a pairing distortion is likely to occur or not, as we did for the *para*-phenylene-coupled polymer.

As indicated in Schemes 4 and 5, the orbitals of the narrow bands are very similar to the π NBMOs of *meta*-quinodimethane **2**, shown previously in Scheme 1. The alternant/nonalternant classification applies to extended systems as well. Since the orbitals have high coefficients only at the starred atoms (which is one of the interesting characteristics of π NBMOs of odd alternant hydrocarbons and non-Kekulé hydrocarbons[64]), there is neither bonding nor antibonding coupling between neighboring (starred and unstarred) atoms. This is in remarkable contrast to the orbitals of **3** (X = HC$^\cdot$), shown above in Schemes 2 and 3. If the geometry is then distorted, the degeneracy at the Fermi level is hardly removed, because to a first approximation the energy of the lower branch will not be stabilized nor the upper branch destabilized, owing to nearest neighbor interactions. More distant interactions will produce a tiny splitting.

We conclude that a pairing or Peierls distortion is unlikely to occur in the *meta*-linked polymer **4** (X = HC$^\cdot$). In fact, it is impossible to draw a satisfactory half-quinonoid valence-structure in the *meta*-phenylene-coupled polymer, as indicated in **10**.



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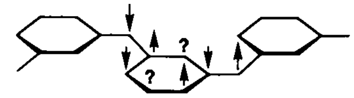
The antiferromagnetic (SDW) state of **4** (X = HC$^\cdot$) is also less likely than the ferromagnetic state, as a consequence of a spin-polarization effect. In the antiferromagnetic state, spin frustration must occur somewhere in the phenyl rings, as indicated schematically in **11**. Such spin frustration is destabilizing from the viewpoint of DODS (different orbitals for different spins) wavefunctions,[65] the spin-up part of which is substantial on the starred atoms and the spin-down part of which is distributed over the unstarred atoms, owing to electron correlation. This DODS picture is similar to the VB picture. Exchange interaction in this polymer is clearly strong, since the orbitals are coextensive in the bridge moieties, as was shown in Schemes 4 and 5. We anticipate the ferromagnetic state of the *meta*-linked polymer will be more stable than the antiferromagnetic state.



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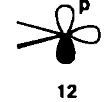
That the ground state of this polymer is expected to be ferromagnetic does not contradict a Peierls' prediction that a metallic state of one-dimensional systems is unstable.[42] This is because this polymer prefers to become a magnetic rather than a nonmagnetic insulator, in contrast to **3** (X = HC$^\cdot$), which prefers a nonmagnetic insulating state. In fact, since the effective mass of an electron in a narrow band is large, this polymer is not likely to become a good electrical conductor even on doping. As indicated by Whangbo,[61c] electrons of a magnetic insulating state are to be regarded as localized, which implies no interaction between electrons of neighboring sites and vanishing bond order between nearest neighbor sites. Narrow bands are a direct consequence of this suggestion. We may add a comment: "no interaction" does not mean the absence of all interaction—in order to achieve ferromagnetic coupling, electrons must be highly overlapped in space to increase exchange interactions, although their "net overlap" must be zero or nearly so, as mentioned above. Differential overlap in $(ab|ba)$ is essential for substantial exchange interactions. This is an important result of Equation (1).[50]

Band Structure of Poly(*meta*-phenylcarbene): A linear methylene (CH_2) molecule has two degenerate perpendicular 2p orbitals into which two electrons are placed.[66] On bending from a linear geometry, one of the 2p orbitals (we call it σ), the one in the molecular plane, mixes with the 2s orbital on carbon, and as a result is slightly stabilized in energy. The other 2p orbital, perpendicular to the molecular plane, is to a first approximation unaffected by the bending, as indicated in **12**. We will denote this orbital as p, or at times, when it is part of a conjugated system, as π. A general description of the electronic structure of carbenes may be based on this simple picture.[66] Four electronic configurations arise from populating σ and p by two



12

electrons. The ground state of CH_2 itself is a triplet, somewhat bent. Other carbenes may have singlet or triplet ground states, with a variable degree of bending at the carbon in each state.

Poly(*meta*-phenylcarbene) **4** (X = C$^{\cdot\cdot}$), is perhaps the most intriguing conjugated linear-chain polymer, one with potential as a possible organic ferromagnet. High-spin states up to $S = 9$ of the oligomers of this important structure have been synthesized and characterized by Iwamura et al.[67] This is the highest-spin state known for a single organic molecule. Hartree–Fock calculations of this polymer were reported in refs. [38] and [39a].

Let us now look at the band structure and DOS of **4** (X = C$^{\cdot\cdot}$, C-X-C angle of 140°) with a planar structure. Four narrow bands appear (we can actually see only three) near the Fermi level, as shown in Figure 9. The two lower bands are exactly like the π NBMO bands of **4** (X = HC$^{\cdot}$) and are nearly degenerate, as discussed above. The shaded area of the central DOS is the contribution from all π bands; that of the DOS on the right is the contribution from just the 2p or π orbitals at the methylene centers. The upper two bands of the set near the Fermi level originate from a well-localized σ orbital in the bridge, the extended structure analogue of σ in **12**.

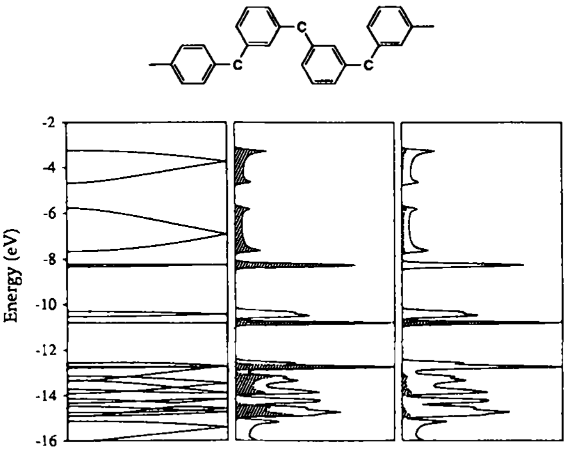
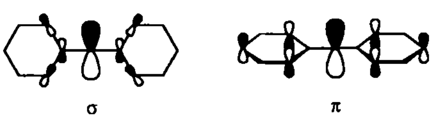


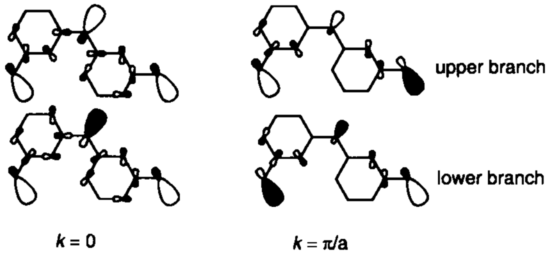
Fig. 9. Band structure and DOS of poly(*meta*-phenylcarbene) with the planar structure. The shaded area of the first DOS (center) is the contribution from π bands, and that of the second DOS (right) is the contribution just from the π orbitals at the methylene centers.

As discussed by one of us earlier for diphenylcarbene, a reasonable model for the polymer,[66] the order of the σ and π MOs is the result of a delicate balance. Although it is difficult to determine the order of these orbitals from qualitative calculations, one simple picture of diphenylcarbene and its polymer is as follows: in a hypothetical "linear" structure, the σ MO lies well above the p (π) MO, owing to antibonding mixing with phenyl ring σ orbitals, as shown in Scheme 6. On bending, the σ MO is stabilized by mixing in 2s character on the central carbon, while the π MO goes up. At the bridging angle of 140° which we assume in our model calculation, the σ MO lies slightly above the π MO. This is the order we see in Figure 9.



Scheme 6.

The difference between the band structure of **4** (X = HC$^{\cdot}$) and that of **4** (X = C$^{\cdot\cdot}$) resides only in the existence of the narrow σ bands, as anticipated. The σ orbital is localized mostly in the bridge moiety, as indicated in Scheme 7. Thus methylene (CH_2) itself might serve as a model for the electronic interactions. The best theoretical estimate of the singlet–triplet splitting of methylene (CH_2) is about 10 kcal mol^{-1} (triplet ground state), in agreement with the observed structure.[51] Since the π NBMO and this σ orbital are very much coextensive in the bridge moiety, exchange interactions (πσ|σπ) should be large between electrons in both bands. Consequently we expect that electrons in the two bands will interact ferromagnetically.



Scheme 7.

Although this π–σ interaction is often compared to the s–d interaction in metals, this may not be an apt analogy, because both the π and σ electrons in **4** (X = C$^{\cdot\cdot}$) are well-localized and their bandwidths are extremely narrow. Consequently the π electrons of **4** (X = C$^{\cdot\cdot}$) do not contribute to electrical conduction; this situation is quite different from that of the s bands of metals. On the other hand, the π band of polyacetylene is about 10 eV wide[41b, 8] and rather similar to the s bands of metals.[44] We think the s–d interaction in metals resembles the magnetic interaction in "pendant-type" organic magnets such as poly(phenoxyacetylene).[39d]

Helical Geometries of Poly(*meta*-phenylcarbene): In Figure 10 left, we show the DOS of **4** (X = C$^{\cdot\cdot}$), now with the 3-fold helical structure with $\tau_{1-2-3-4} = \tau_{2-3-4-5} = 23.5°$ shown previously

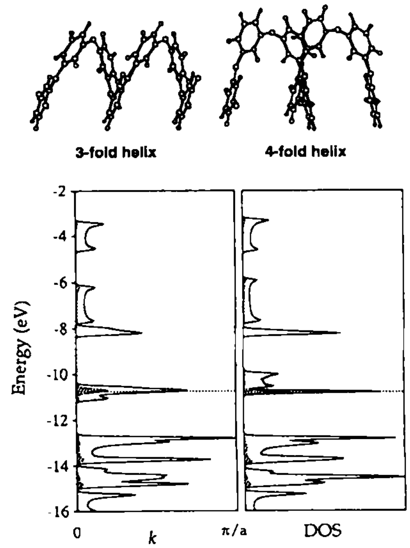


Fig. 10. DOS profiles of poly(*meta*-phenylcarbene) with 3-fold (left) and 4-fold (right) helical structures. The DOS projections are the contribution from the pseudo-π orbitals at the methylene centers.

in Figure 7. The shaded area identifies the contribution from pseudo-π orbitals at the methylene centers to the total DOS. Although the C-X-C angle of 130° in this helical structure is a little small for the methylene case, the DOS profiles of Figures 9 and 10 are quite similar. The essential physical point of this band structure is the strongly localized nature of the two kinds of electrons at the methylene centers, a consequence of the *meta*-phenylene-coupled geometry.

As mentioned above, the C-X-C angle of 130° is not ideal for the diphenylcarbene coupled polymer. Triplet carbenes prefer a more open angle. Figure 11 shows a beautiful periodic 4-fold helical structure.[68] The unit cell of this structure contains four benzene rings and four carbenes. In a 4-fold helical structure, there is also a relation between θ and τ [Eqn. (5)], where

$$\{2\pi-(\theta+120^\circ)\}/\cos\tau = 90^\circ \quad (5)$$

$\theta > 150^\circ$. Subject to this constraint, we optimized θ and τ at $\theta = 153^\circ$ and $\tau_{1-2-3-4} = \tau_{2-3-4-5} = 14.8^\circ$, respectively. The bridging angle of 153° is perhaps more appropriate than 130° in the 3-fold structure, because the observed value of the bridge angle in diphenylcarbene, from ESR and ENDOR, is 140–150°.[52] Since in the 4-fold helical structures the steric problems caused by the *ortho*-hydrogens' contacts are diminished still further, the optimized dihedral angle is smaller than the value we found for the 3-fold helical structure. The distance between the *ortho*-hydrogens of neighboring benzene rings is 2.4 Å; there is no steric problem at all in this structure. We believe that this 4-fold structure is a satisfactory periodic model for polymer 4 ($X = C^{\bullet\bullet}$). The structure of this polymer is not clear (only oligomers are known so far); it will be very interesting to see its geometry when it is made.

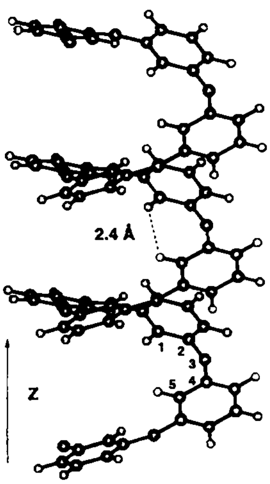


Fig. 11. 4-fold helical geometry of poly(*meta*-phenylcarbene). Dihedral angles, $\tau_{1-2-3-4} = \tau_{2-3-4-5} = 14.8^\circ$.

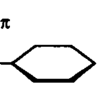
Figure 10 right shows the DOS of 4 ($X = C^{\bullet\bullet}$) with this 4-fold helical structure. In the band structure (not shown here) all of the bands are folded back three times at the zone center and the zone edge; this is also a direct consequence of the 4_1 screw axis.[44] The projection in the DOS identifies the contribution from pseudo-π orbitals at the methylene centers. The DOS profiles of Figure 10 left and right are quite similar.

As we argued for 4 ($X = HC^{\bullet}$), the localized orbital patterns, shown in Schemes 4 and 5, are unlikely to provide a driving force for a pairing distortion. We think this polymer is likely to be a ferromagnetic rather than a nonmagnetic insulator.

Polymers Containing Nitrogen-Based Radicals Coupled through the *meta*-Phenylene Unit: Nitrogen-based radicals such as aminyl ($N^{\bullet}$), aminium ($HN^{\bullet +}$), and nitroxide ($NO^{\bullet}$) are often stable organic radicals,[69] and thus also interesting as potential spin carriers of organic ferromagnets. In fact, aminyl and aminium radicals are isoelectronic to the methyl radical discussed above. Moreover, nitroxide has a π^* singly occupied MO (SOMO), the unique nodal properties of which play an important role in ferromagnetic intermolecular coupling in certain specific stacking modes.[50] Several experimental studies of the ferromagnetic interactions of nitrogen-based radicals coupled by a *meta*-phenylene unit have been carried out so far.[12, 15–17]

We have carried out calculations for 4 ($X = N^{\bullet}$, $HN^{\bullet +}$, and $NO^{\bullet}$) with planar and helical structures. The expected narrow bands, appropriate for the appearance of ferromagnetic interactions, appear at the Fermi level in each case. We will show the band structure of only one of these, but let us discuss them in turn.

The poly(*meta*-phenyleneaminylene) polymer 4 ($X = N^{\bullet}$) has a local electronic structure shown in **13**. The band structure, not shown here, reveals narrow bands for both planar and helical structures, very similar to the corresponding carbene species (but occupied by one more electron).



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Next we consider a chain of aminium radicals ($HN^{\bullet +}$) coupled through a *meta*-phenylene unit, again with planar and helical structures. The polymer in question has been prepared by oxidizing its neutral form, which we call poly(*meta*-aniline),[16] with iodine as a dopant; however, the observed spin concentration was small and the ferromagnetic interaction weak and local. The small spin concentration is probably due to the large electrostatic repulsion in this cationic form.

The computed band structure of this polymer, also not shown here, in both planar and helical forms resembles that of the isoelectronic $HC^{\bullet}$ system **8** (Figs. 6 and 8). The only difference is that the nonbonding band for the $HN^{\bullet +}$ case is wider, namely 0.34 eV. This should weaken the anticipated preference of this polymer for a ferromagnetic ground state. But we think a pairing distortion, if it occurs, is probably slight.

Finally we look at the band structure and DOS of nitroxides coupled through a *meta*-phenylene unit in planar (**14**) and helical polymer structures.

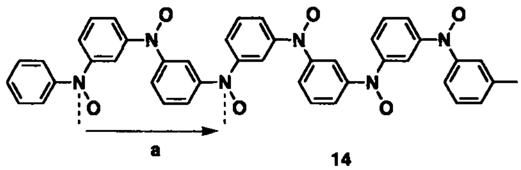

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Figure 12 shows the band structure and DOS of this polymer. The orbitals of the magnetic bands (the folded-back half-occu-

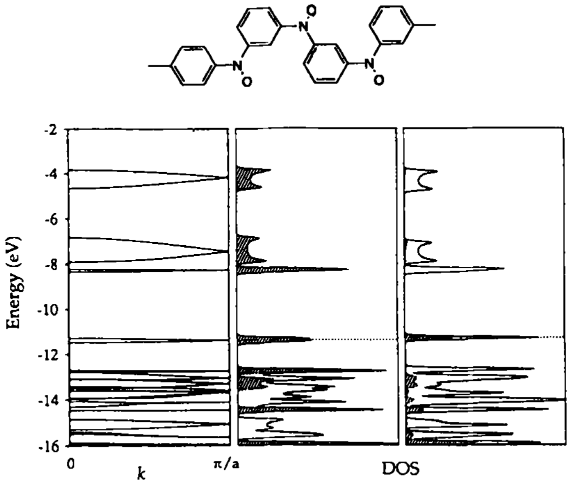


Fig. 12. Band structure and DOS (center) of the planar polymer with nitroxide ($NO^{\bullet}$) radicals coupled through a *meta*-phenylene unit. The projection of the first DOS (center) is the contribution from π bands. That in the second DOS (right) shows the contribution just from the pseudo-π orbitals at the radical centers (N and O) of the 3-fold helical structure.

pied band at −11.3 eV) are well-localized on the nitroxide moieties (π* SOMO) as well as on the starred atoms. The magnetic bands are thus well separated from other bands. Since nitroxide is chemically stable, this polymer seems to us to have great potential as a nitrogen-based linear-chain organic ferromagnet. Also from the viewpoint of interchain interaction, this polymer is interesting, because the π* SOMO of nitroxide has a chance to exhibit ferromagnetic coupling between chains, as discussed previously.[50]

Summary

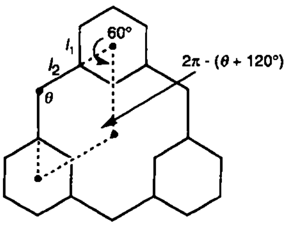
We have discussed the structural and electronic properties of several conjugated linear-chain polymers based on radical sites coupled through benzene rings. Electronic and magnetic strucatures were considered for polymers with *para*-phenylene and *meta*-phenylene coupling units. Nonplanar as well as planar geometries were taken into account, and two novel helical structures were suggested. Throughout, our discussion has focused on the concept of a possible pairing distortion, sometimes found, sometimes judged unlikely. This is one of several vantage points on these intriguing materials.

In the polymer with methyl radicals coupled through a *para*-phenylene unit, a metallic state should be unstable, and a pairing or Peierls distortion occurs to remove the degeneracy at the Fermi level. This is a typical metal–insulator transition in one-dimensional electronic systems, very much like that of polyacetylene. However, since this polymer has a relatively small bandgap (1.33 eV)—owing to the small HOMO–LUMO gap of the parent *para*-quinodimethane **1**—the polymer is interesting as a potential conducting material.

On the other hand, in the polymers with methyl radicals, carbenes, and nitrogen-based radicals coupled through a *meta*-phenylene unit 4 distinctive half-occupied narrow bands with π NBMO character appear at the Fermi level. In these polymers, a ferromagnetic state should be stable, compared with metallic, off-diagonal CDW (Peierls), and SDW states. We argue that this type of polymer is likely to be a magnetic rather than nonmagnetic insulator. Since the orbitals of magnetic bands of the polymers with a *meta*-phenylene coupling unit are extensive on the starred atoms, especially on the bridge moieties, conditions for ferromagnetic interaction are fulfilled in this structure. We have discovered novel 3-fold and 4-fold helical structures for these polymers.

Method of Calculation

The C–C bond length of a benzene ring was set at 1.40 Å, and those of a quinonoid ring at 1.481 and 1.344 Å (from the values of *para*-benzoquinone). The C–C bond length of the bridge moiety was taken to be 1.42 Å, except for **9** (1.46 and 1.38 Å). The C–H, N–H, and N–O bond lengths were set at 1.08, 1.01, and 1.27 Å, respectively. The bridging (C-X-C) angle was assumed to be 140° in all planar geometries. All other bond angles were taken as 120°, except for **7**.



Scheme 8: Projection of 3-fold helix along the polymer axis (actual rather than projected angles and distances are shown).

The relation between the bridge angle (θ) and the torsion angle (τ) in the 3- and 4-fold helices of *meta*-phenylene-coupled polymers can be obtained from Scheme 8 (a projection of the 3-fold helix along the polymer axis). l_1 (1.40 Å) and l_2 (1.42 Å) are the C–C bond lengths of the benzene ring and the bridge moiety, respectively. To generate the 3-fold helix, it is necessary that $\{2\pi-(\theta+120°)\}/\cos\tau$ should be 120°. Similarly, $\{2\pi-(\theta+120°)\}/\cos\tau$ should be 90° for the 4-fold helix.

The following atomic parameters were used in the extended Hückel calculations (H_{ii}, orbital energy; ζ, Slater exponent): C 2s, −21.4 eV, 1.625; C 2p, −11.4 eV, 1.625; N 2s, −26.0 eV, 1.950; N 2p, −13.4 eV, 1.950; O 2s, −32.3 eV, 2.275; O 2p, −14.8 eV, 2.275; H 1s, −13.6 eV, 1.3. 40 k points were typically used for the band calculations in the range [0, π/a], and 50 k points for the DOS calculations.

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