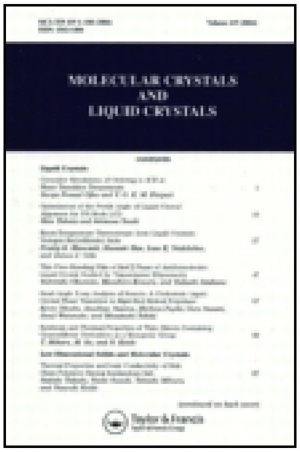

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New Designs for Organic Molecules and Materials with Novel Magnetic Properties

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NEW DESIGNS FOR ORGANIC MOLECULES AND MATERIALS WITH NOVEL MAGNETIC PROPERTIES

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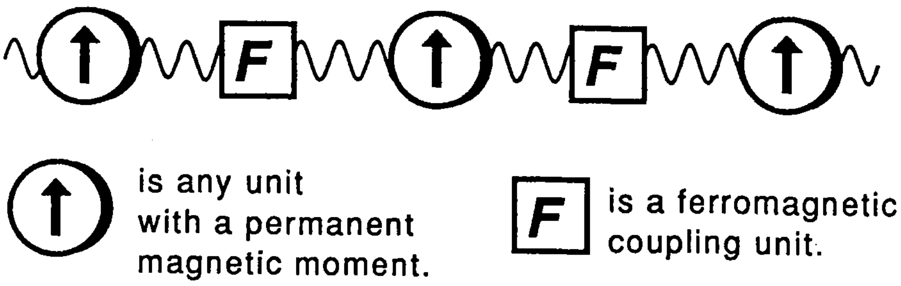
Abstract The synthesis and preliminary doping studies of a new polymer designed to test the viability of "polaronic ferromagnetism" are described.

The pursuit of molecular-based materials with novel magnetic properties has developed into a major focus of modern chemistry.[1] Both inorganic[2-4] and organic[5,6,7] chemists are attempting to rationally design structures that display cooperative magnetic behaviors in the solid state. Some success has been seen with inorganic crystalline materials, most notably the Mn-Cu systems of Kahn[2] and the Mn-nitronylnitroxide systems of Gatteschi.[3] In the organic area, a crystalline charge transfer complex of decamethylferrocene with TCNE has been shown by Miller and coworkers[5] to be ferromagnetic below 5 K, and other workers[6] are pursuing crystalline, organic charge-transfer systems that could display bulk ferromagnetic behavior. In addition, the stable organic radical galvinoxyl displays strong ferromagnetic coupling in the crystalline state.[7] Since ferromagnetism is a bulk property requiring cooperative behavior in three dimensions, the precise arrangement of molecules within a crystal determines whether inter-stack and intermolecular couplings are ferromagnetic or antiferromagnetic. This, in turn, determines the bulk magnetic properties of the material, and so control of crystal packing patterns represents a major challenge for these efforts.

An alternative approach involves the construction of larger organic molecules with many unpaired spins. There are now several "recipes" for controlling the coupling of unpaired spins in organic systems. Spectacular examples of very high spin structures have emerged from the groups of Itoh and Iwamura[8] and others.[9] As such structures get larger, eventually one is considering polymers,[10] and several theoretical models[11] for the construction of potentially ferromagnetic polymers have been presented. An advantage to this approach is that along the polymer backbone, exchange interactions (and hence high-spin preferences) among spins might be larger than those experienced by molecules in a crystal lattice with minimal direct overlap.[12] In addition, the favorable materials properties of polymers will likely have significant advantages over crystalline materials for certain applications. However, controlling *inter*chain spin coupling, as must be done to achieve bulk magnetic behaviors, will likely be at least as challenging in the polymer systems as it is for the crystalline structures.

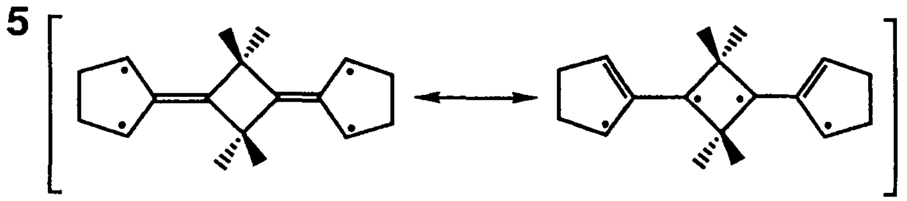
Our own interests are in the preparation of a polymer-based, organic ferromagnet, and we will summarize some of our more recent efforts here. "Organic Ferromagnets" is a phrase that will see much usage in coming years, but it is important to realize that there are many types of magnetic order.[14] In any solid containing a large number of unpaired electrons, a wide array of magnetic phenomena may be observed, depending on the extent of the electron-electron interactions and whether pairwise interactions are ferro- or antiferromagnetic. In a polymer, most of the fourteen types of magnetism reviewed by Hurd[14] would appear to be feasible. Thus, while pursuing a ferromagnet, one must be alert to the possibility that a spin glass, asperomagnet, or some other novel type of magnetic system might arise.

We have previously described[15] our schematic approach to potentially ferromagnetic polymers. Structure **1** conceptually divides the problem into a search for two types of building blocks: a spin-containing unit and a ferromagnetic coupling unit. Much progress has been made in the development of potentially general ferromagnetic coupling units. By far, the best documented case is "meta through a benzene". That is, two spin-containing species that are linked to the 1,3-positions of a benzene are high-spin (ferromagnetically) coupled. The very high spin polycarbene systems[8] dramatically illustrate this point. It has also been shown that such coupling can be seen with simple monoradicals[9,16] and, in our own work, delocalized biradicals.[15]



1

We have proposed[15,17] that localized 1,3-biradicals such as cyclobutanediyls[18] and cyclopentanediyls[19] can also serve as general ferromagnetic coupling units. As a test of this, we designed tetraradical 2, in which two derivatives of trimethylenemethane (TMM)[20] are coupled through a cyclobutanediyl. We have recently prepared this structure and shown that it does, in fact, have a quintet ground state, thereby establishing that there is ferromagnetic coupling between the two TMMs.[21] Structure 2 is the first rationally designed organic quintet that does not owe its high spin preference to the topology of a delocalized π system. We anticipate many new efforts will be directed toward the design of general ferromagnetic coupling units.



2

Recently, we have begun to address the possible use of a novel type of spin-containing unit. Ideally, one would like any organic ferromagnet to be as thermally and environmentally stable as possible. Our interest in the conducting polymers area[22] lead us to consider polarons as a potentially quite stable, spin-containing unit. One can think of a polaron as a radical cation (radical anion) obtained upon oxidative (reductive) doping of a conjugated polymer. It seemed to us that under appropriate conditions one might be able to high-spin couple polarons to make an interesting polymer system. As we were considering this possibility, we became aware of the important work of Fukutome[23] which included a detailed, quantitative analysis of the problem and coined the phrase "polaronic ferromagnetism". Fukutome's results clearly indicated the potential of such an approach, and we describe herein our first efforts at construction of a system that could display polaronic ferromagnetism.

Based upon considerations of synthetic feasibility, ease of doping, Fukutome's analysis, and the generality of high-spin meta coupling, we settled on structure **3** as our first target. Oxidative doping will occur at the polyene fragment to give the desired radical cation (polaron). Polymer **3** raises several critical questions.

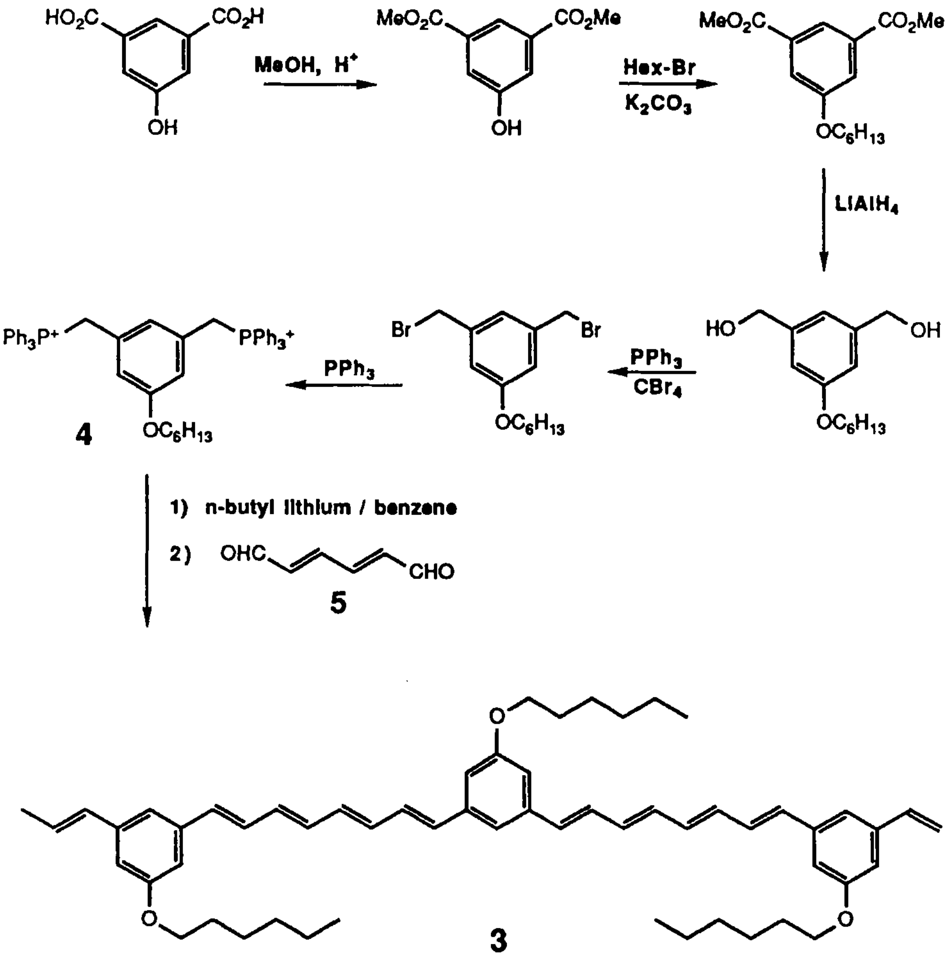
(1) Can such structures be readily synthesized?
(2) Can one produce a high density of polarons and prevent their annihilation to bipolarons?
(3) Is the one-dimensional coupling ferromagnetic?
(4) Can three-dimensional ordering be obtained?

Concerning the second question, the general model[24] for the nature of the carriers in doped conducting polymers invokes polarons at light doping levels. However, as doping continues, polarons combine or annihilate each other to produce spinless bipolarons (dications). Of course, bipolaron formation would subvert any attempt to make a polaronic ferromagnet.

The basic synthetic approach (Scheme) uses a Wittig condensation of a bis-ylide with the readily available muconaldehyde **5**. Our initial efforts used a phosphonium salt related to **4** but without the O-hexyl group, prepared in one step from commercially available xylylenedibromide. "Polymerization", however, was not very successful, as all data indicated the formation of only insoluble dimers and trimers.

Based on extensive precedent from the conducting polymers field,[25] we reasoned that solubility was a major factor in limiting the extent of polymerization. We therefore added hexyloxy groups to increase solubility. The requisite phosphonium salt (**4**) was synthesized as shown in the Scheme. Polymerization now proceeded much more smoothly to produce initially both a benzene-soluble portion and an insoluble portion.

SCHEME


HO2C
CO2H
OH
MeOH, H+
MeO2C
CO2Me
OH
Hex-Br
K2CO3
MeO2C
CO2Me
OC6H13
LiAlH4
HO
OH
OC6H13
PPh3
CBr4
Br
Br
OC6H13
PPh3
Ph3P+
PPh3+
4
OC6H13
1) n-butyl lithium / benzene
2) OHC CHO
5
O
O
O
3

The initial *soluble* portion was analyzed by NMR and IR to confirm its basic composition. GPC analysis (polystyrene standard) gave $M_N = 1600$; $M_W = 2200$, suggesting the formation of 6- to 8-mers (monomer weight = 280). Soxhlet extraction (benzene) of the insoluble portion gave a second soluble portion which, by GPC, had $M_N = 1800$ $M_W = 2600$. Note that the monomer unit of 3 has 11 (or 13, depending on how the benzene is counted) sp^2 carbons along the chain, so even modest oligomers have a significant "conjugation" length.

The data we have on the insoluble portion suggests that it is essentially higher molecular weight 3. Elemental analysis/end-group considerations suggest that 8- or 9-mers may be typical, but with a substantial amount of the material corresponding to significantly higher oligomers. Thus, in answer to the first question, we believe such polymers can be made by Wittig condensation. With more proficient solubilizing groups, we expect that even higher molecular weights will be obtained.

Preliminary doping experiments with the *insoluble* portion have been encouraging. A variety of studies on conducting polymers such as polypyrrole, poly(p-phenylene), and polydithiophene produce a consistent picture.[24] At low doping levels, the number of spins (as measured by EPR) increases with increased doping, consistent with polaron formation. On further doping – or simply on allowing the sample to stand 10^3-10^4 sec – the EPR signal intensity drops significantly and in some systems is completely lost. This is taken to indicate bipolaron formation by polaron combination and/or polaron ionization.

The doping behavior (AsF_5; gas phase) of 3 appears to be qualitatively different. Exposure to dopant leads to a rapid rise in spin concentration, followed by a leveling off of EPR signal intensity to a final value which depends on the pressure of AsF_5 used. In the presence of dopant, this signal appears to be indefinitely stable. If the AsF_5 is pumped off, there is an initial drop in EPR intensity, but a substantial fraction of the spins remains even after periods as long as 12 days at room temperature. Additional EPR and magnetic susceptibility studies are in progress.

These observations are certainly consistent with our model, in which bipolaron formation is suppressed in 3. We hasten to add, however, that these are very recently obtained results, and that other explanations are possible. Perhaps doping leads to extensive cross-linking, which prevents bipolaron formation. Or perhaps the maximum doping level achieved (believed to be *ca.* 4% monomers oxidized) is insufficient to observe bipolarons. We consider these results to be encouraging, but certainly much more work remains before it can be established that polaronic ferromagnetism will be experimentally realizable.

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References

1. Symposium on Ferromagnetic and High Spin Molecular Based Materials; 197th American Chemical Society National Meeting; April 9-14, 1989; Dallas, TX, USA. Proceedings: *Mol. Cryst. Liq. Cryst.*, in press.
2. O. Kahn, Y. Pei, M. Verdaguer, J.P. Renard, and J. Sletten, *J. Am. Chem. Soc.* 110, 782 (1988). K. Nakatani, J.Y. Carriat, Y. Journaux, O. Kahn, F. Lloret, J.P. Renard, Y. Pei, J. Sletten, and M. Verdaguer, *J. Am. Chem. Soc.* 111, 5739 (1989).
3. A. Caneschi, D. Gatteschi, J. Laugier, P. Rey, R. Sessoli, and C. Zanchini, *J. Am. Chem. Soc.* **110**, 2795 (1988). A. Caneschi, D. Gatteschi, J.P. Renard, P.Rey, and R. Sessoli, *J. Am. Chem. Soc.* **111**, 785 (1989).
4. A. Bino, D.C. Johnston, D.P. Goshorn, T.R. Halbert, and E.I. Stiefel, *Science* **241**, 1479 (1988). P.D.W. Boyd, Q. Li, J.B. Vincent, K. Folting, H.-R. Chang, W.E. Streib, J.C. Huffman, G. Christou, and D.N. Hendrickson, *J. Am. Chem. Soc.* **110**, 8537 (1988).
5. J.S. Miller, J.C. Calabrese, H. Rommelmann, S.R. Chittipeddi, J.H. Zhang, W.M. Reiff, and A.J. Epstein, *J. Am. Chem. Soc.* **109**, 769 (1987). J.S. Miller, A.J. Epstein, and W.M. Reiff, *Acc. Chem. Res.* **21**, 114 (1988). J.S. Miller, A.J. Epstein, and W.M. Reiff, *Chem. Rev.* **88**, 201 (1988).
6. (a) J. Thomaides, P. Maslak, R. Breslow, *J. Am. Chem. Soc.* **110**, 3970 (1988). T.J. LePage, R. Breslow, *J. Am. Chem. Soc.* **109**, 6412 (1987). F. Wudl, G. Srdanov, B. Rosenau, D. Wellman, K. Williams, S.D. Cox, and V. Yoon, *Pure Appl. Chem.* **59**, 975 (1987). (b) L.Y. Chiang, D.C. Johnston, D.P. Goshorn, and A.N. Bloch, *J. Amer. Chem. Soc.* **111**, 1925 (1989). J.B. Torrance, P.S. Bagus, I. Johannsen, A.I. Nazzal, S.S.P. Parkin, and P. Batail, *J. Appl. Phys.* **63**, 2962 (1988).

7. K. Awaga, T. Sugano, and M. Kinoshita, *J. Chem. Phys.* **85**, 2211 (1986).
8. K. Itoh, *Chem. Phys. Lett.* **1**, 235 (1967). E. Wasserman, R.W. Murray, W.A. Yager, A.M. Trozzolo, and G. Smolinsky, *J. Am. Chem. Soc.* **89**, 5076 (1867). T. Sugawara, S. Bandow, K. Kimura, H. Iwamura, and K. Itoh, *ibid.* **108**, 368 (1986). K. Itoh, T. Takui, Y. Teki, and T. Kinoshita, *J. Mol. Electronics* **4**, 181 (1988). S. Murata, T. Sugawara, and H. Iwamura, *J. Am. Chem. Soc.* **109**, 1266 (1987). A. Izuoka, S. Murata, T. Sugawara, and H. Iwamura, *J. Am. Chem. Soc.* **109**, 2631 (1987).
9. D.E. Seeger, P.M. Lahti, A.R. Rossi, J.A. Berson, *J. Am. Chem. Soc.* **108**, 1251 (1986).
10. Y.V. Korshak, T.V. Medvedeva, A.A. Ovchinnikov, and V.N. Spector, *Nature* **326**, 370 (1987). See also ref. 6b.
11. See for example, A.A. Ovchinnikov, *Theor. Chim. Acta* **47**, 297 (1978). D.J. Klein, C.J. Nelin, S. Alexander, and F.A. Matsen *J. Chem. Phys.* **77**, 3101 (1982). N. Tyutyulkov, P. Schuster, and O. Polansky, *Theoret. Chim. Acta (Berl.)* **63**, 291 (1983). N. Tyutyulkov, O.E. Polansky, P. Schuster, S. Karabunarliev, and C.I. Ivanov, *Theoret. Chim. Acta (Berl.)* **67**, 211 (1985). N.N. Tyutyulkov and S.C. Karabunarliev, *Intl. J. of Quantum Chem.* **24**, 1325 (1986). C.I. Ivanov, N.Tyutyulkov, G. Olbrich, H. Barentzen, and O.E. Polansky, *Theor. Chim. Acta* **73**, 27 (1988). O.E. Polansky, P. Schuster, C.I. Ivanov, and N. Tyutyulkov, *Intl. J. of Quantum Chem.* **32**, 491 (1987).
12. "Exchange equals overlap" [13]
13. D.C. Mattis "The Theory of Magnetism I. Statics and Dynamics" (Springer-Verlag, Berlin, 1988), p 41.
14. For an excellent review of the many types of magnetism, see C.M. Hurd, *Contemp. Phys.* **23**, 469 (1982).
15. D.A. Dougherty, *Mol. Cryst. Liq. Cryst.*, in press.
16. M. Rule, A.R. Matlin, E.F. Hilinski, D.A. Dougherty, and J.A. Berson, *J. Am. Chem. Soc.* **101**, 5098 (1979). V.P. Senthilnathan and M.S. Platz, *ibid.*, **102**, 7637 (1980).
17. D.A. Dougherty, *Pure and Appl. Chem.*, in press.
18. R. Jain, M.B. Sponsler, F.D. Coms, and D.A. Dougherty, *J. Am. Chem. Soc.* **110**, 1356 (1988). M.B. Sponsler, R. Jain, F.D. Coms, and D.A. Dougherty, *J. Am. Chem. Soc.* **111**, 2240 (1989).
19. F.D. Coms and D.A. Dougherty, *Tetrahedron Lett.* **29**, 3753 (1988). S.L. Buchwalter and G.L. Closs, *J. Am. Chem. Soc.* **101**, 4688 (1979).
20. P. Dowd, *Acc. Chem. Res.* **5**, 242 (1972). J.A. Berson, *Acc. Chem. Res.* **11**, 446 (1978).
21. J.A. Novak, R. Jain, and D.A. Dougherty, *J. Am. Chem. Soc.* **111**, 7618 (1989).
22. J. Pranata and D.A. Dougherty, *J. Am. Chem. Soc.* **109**, 1621 (1987). J. Pranata and D.A. Dougherty, *Syn. Metals* **22**, 171 (1987). J. Pranata, R.H. Grubbs, and D. A Dougherty, *J. Am. Chem. Soc.* **110**, 2973 (1988). T.M. Swager, D.A. Dougherty, and R.H. Grubbs, *J. Am.*

Chem. Soc. **110**, 2973 (1988). J. Pranata, V.S. Marudarajan, and D.A. Dougherty, *J. Am. Chem. Soc.* **111**, 2026 (1989).

23. H. Fukutome, A. Takahashi, and M. Ozaki, *Chem. Phys. Lett.* **133**, 34 (1987).

24. J.C. Scott, J.L. Brédas, J.H. Kaufman, P. Pfluger, G.B. Street, and K. Yakushi, *Mol. Cryst. Liq Cryst.* **118**, 163 (1985). J.H. Kaufman, N. Colaneri, J.C. Scott, K.K. Kanazawa, and G.B. Street, *Mol. Cryst. Liq. Cryst.* **118**, 171 (1985). J.C. Scott, P. Pfluger, M.T. Krounbi, and G.B. Street, *Phys. Rev.* **B28**, 2140 (1983). L.D. Kispert, J. Joseph, G.G. Miller, and R.H. Baughman, *Mol. Cryst. Liq. Cryst.* **118**, 313 (1985). J.H. Kaufman, N. Colaneri, J.C. Scott, and G.B. Street, *Phys. Rev. Lett.* **53**, 1005 (1984). J.C. Scott, J.L. Bredas, K. Yakushi, P. Pfluger, and G.B. Street, *Syn. Metals* **9**, 165 (1984). F. Devreux, F. Genoud, M. Nechtschein, and B. Villeret, in "Electronic Properties of Conjugated Polymers" (Springer-Verlag, Berlin, 1987) p 270. M. Schärli, H. Kiess, G. Harbeke, W. Berlinger, K.W. Blazey, and K.A. Müller, *ibid.*, p. 277.

25. J.P. Aimé, F. Bargain, M. Schott, H. Eckhardt, R.L. Elsenbaumer, G.G. Miller, M.E. McDonnell, and K. Zero, *Syn. Metals* **28**, C407 (1989). K.-Y. Jen, G.G. Miller, R.L. Elsenbaumer, *J. Chem. Soc., Chem. Commun.*, 1346 (1986). M. Sato, S. Tanaka, and K. Kaeriyama, *J. Chem. Soc., Chem. Commun.*, 873 (1986). A.O. Patil, Y. Ikenoue, F. Wudl, and A.J. Heeger, *J. Am. Chem. Soc.* **109**, 1858 (1987). S.H. Askari, S.D. Rughooputh, and F. Wudl, *Syn. Metals* **29**, E129 (1989).