Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Electronic Structure and Magnetic Properties of Some Possible Organic Ferromagnetic Polymers

K. Nath [a] & P. L. Taylor [a]
[a] Department of Physics, Case Western Reserve University, Cleveland, OH, 44106
Version of record first published: 24 Sep 2006.

To cite this article: K. Nath & P. L. Taylor (1991): Electronic Structure and Magnetic Properties of Some Possible Organic Ferromagnetic Polymers, Molecular Crystals and Liquid Crystals, 205:1, 87-100

To link to this article: http://dx.doi.org/10.1080/00268949108032079

Mol. Cryst. Liq. Cryst., 1991, Vol. 205, pp. 87–100
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Electronic Structure and Magnetic Properties of Some Possible Organic Ferromagnetic Polymers

K. NATH and P. L. TAYLOR

Department of Physics, Case Western Reserve University, Cleveland, OH 44106

(Received December 18, 1989; in final form January 31, 1991)

Electronic structures of some π-bonded purely organic oligomers have been calculated using a semi-empirical method. These oligomers are the precursors of organic ferromagnets, and for sufficiently high molecular weight are expected to take a helical polymeric form. A statistical-mechanical approach has been used to study the magnetic properties of some of these yet-to-be synthesized helical polymers with possible free radicals. The magnetic susceptibility and the specific heat have been calculated within the framework of the Ising model for a helix with number of spins ranging from 2 to 9 per loop of the helix, and for two sets of values of the inter-loop and intra-loop spin-spin interaction.

INTRODUCTION

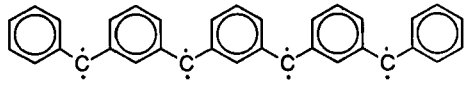
In the search for a purely organic ferromagnet, the principal attention has rightly been paid to the problem of designing molecules having large numbers of unpaired spins. These molecules must also be such that it is energetically favorable for a parallel alignment of these spins to occur.

While these requirements are certainly necessary for organic ferromagnetism, they are not sufficient, and other criteria must be satisfied if useful materials are to be obtained. Practical considerations will probably dictate that organic ferromagnets be synthesized as polymers. An isolated, extended polymer chain is essentially a one-dimensional object, and it is well known that ferromagnetism cannot occur in one dimension. The existence of a non-zero Curie temperature thus depends on the three-dimensional structure of the material.

In this paper we point out that some of the more promising candidates for organic ferromagnetism have polymer chains that are likely to arrange themselves in a helical structure. We examine the electronic bandstructure of one such material in various conformations and then calculate the magnetization and specific heat in the framework of the Ising model. We find a sharp peak in the magnetic susceptibility of these models. This suggests that an assembly of helices of this type would be likely to exhibit ferromagnetism.

STATEMENT OF THE PROBLEM

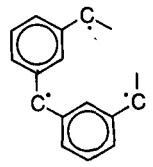
Early attempts to produce a purely organic ferromagnet on a macroscopic scale started over two decades ago when Itoh *et al.*[1] detected a quintet electronic ground state for an aromatic hydrocarbon, *m*-phenylene-bis-phenylmethylene, using an electron spin resonance technique. In 1973 Takui and Itoh[2] observed that benzene-1,3,5-tris-phenylmethylene, an odd alternant hydrocarbon, was in its septet ground state. The group of Itoh and Iwamura[3] have also been able to synthesize a longer oligomer containing four units of carbenes (I) in its nonet electronic ground state, i.e., having eight electrons unpaired. In a recent study[4] (to be referred to as NT) we have used the ASED-MO[5] and ASED-band[6] methods to characterize the electronic structures of these molecules and some other possible organic ferromagnetic linear polymers of carbenes and carbon radicals. The attempt was made to understand the effect of electronic properties on the ferromagnetism of the systems of *s* and *p* electrons only. In NT we also reviewed the previous theoretical and experimental work in this area and concluded that a narrow half-filled band of π-electrons lying between filled valence and empty conduction bands is essential for these electrons to be unpaired. Moreover, favorable topological arrangements of atoms, based on the */non-* criterion of Ovchinnikov,[7] are desirable for these electrons to have their spins aligned parallel and yield a high-multiplicity ground state. The */non-* condition, also known as the spin-up/spin-down criterion, is a simple way of expressing the idea that the exchange interaction between the spins of the π-electrons on nearest neighbor atoms is such as to give antiferromagnetic coupling between them. Odd alternant hydrocarbons with radical or diradical (carbene) carbon atoms placed so as to be second-, fourth-, or sixth-nearest-neighbors to each other are then good candidates to be purely organic ferromagnets. In NT we studied rather simple structures of these hydrocarbons, where only one- or two-dimensional planar arrangements of atoms were considered. As mentioned there, these oligomers or polymers would deviate from straight-line or planar form as a consequence of closed-shell steric repulsion.



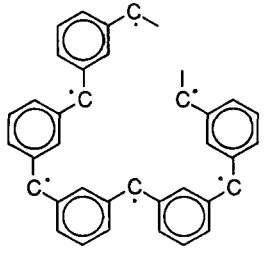
(I)

We have studied some oligomers of carbon radicals (schematic chemical structures II, III, and IV) in the present work and have found that these systems having unpaired spins will have curved shapes. Two methods, to be mentioned shortly, have been used to determine probable conformations, and it has been found that the tendency of a polymer could be to form either helical structures or, less probably, closed rings. Defects or thermal excursions from the lowest-energy conformation could interfere with the formation of a helix in its initial stages; however, once the first loop of helical structure has been completed, succeeding monomers are likely to be readily attracted to the growing site of the helix.

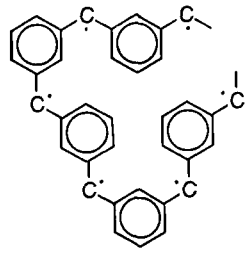
With the supposition that these large helical polymers can be formed, it is natural to ask how large their magnetizability will be. In particular, is an assembly of such helices likely to exhibit a macroscopic ferromagnetic phase transition? We have



(II)



(III)



(IV)

tried to answer this question within the framework of an Ising model,[8] in which the interactions are assumed to be only between the nearest neighbor spins on these radicals or diradicals, and the values these spins can take are either $+1$ or -1 in units of $\hbar/2$. The weak (but long-range) dipole-dipole interactions between spins on different loops of the helix have been approximated by the nearest-neighbor inter-loop interactions in the Ising-model framework.

STRUCTURE OPTIMIZATION

We have used two different methods to achieve a rough optimization of the structure of the $(C_6H_5)_2\dot{C}H$ radical structure as presented in Figure 1. First we have used the ASED-MO method[5] for which the parameters for the ionization potentials and the Slater exponents for the carbon and hydrogen atoms are taken to be the ones reported in NT. The minimum in the total energy, which is the sum of the two-body repulsion energy and the MO energy, corresponds to equal torsional angles α and β of 28°, and a C—Ċ—C bond angle η of 124°. The C—Ċ bond length has

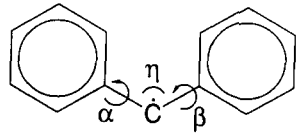


FIGURE 1 The $(C_6H_5)_2\dot{C}H$ radical structure. For the ASED-optimized geometry $\alpha = \beta = 28°$, $\eta = 124°$ and the C—Ċ bond length is 1.43 Å. For the Sybyl-optimized geometry $\alpha = \beta = 29°$, $\eta = 123°$ and the C—Ċ distance is 1.51 Å.

been found in this method to be 1.43 Å. The C—C partial double bond lengths within the phenyl rings and the C—H bond lengths were fixed at 1.40 Å and 1.08 Å respectively, as was done in NT.

In a second independent approach we have used the Maximin2 energy minimizer of the Sybyl^R molecular modeling software from Tripos Associates, Inc. The nature of the carbon atoms in a phenyl ring was chosen to be aromatic and that of the bridging carbon radicals to be of the sp^2 type. The total energy is the sum of the van der Waals and Coulomb energies, plus the energy contribuiton due to chemical bonding. The parameters for the stretching, bending, and torsional force constants in the program are obtained from various *ab initio* and semi-empirical calculations on small molecules. The charges on the atoms within the molecule have been calculated using the Gasteiger-Hückel option. The minimum in the total energy was found to correspond to equal torsional angles α and β of 29°, and a C—Ċ—C bond angle η of 123°. These numbers are within a few per cent of those obtained by the ASED-MO method. The optimized C—Ċ bond length was found to be 1.51 Å, which is 0.08 Å larger than the one obtained using the ASED-MO method. Thus we see that these two methods give more or less the same structure for the diphenylcarbon radical. We do note, however, the limitations of the Sybyl method, which must be considered as only qualitative. The parameters are based on study of much smaller molecules, as mentioned earlier, and refer primarily to the ground state and to closed-shell systems. The method was used in order to build a basic structure which had a reasonable geometry with which to check the conjecture about the magnetic properties.

Of the various structures that can be formed under these constraints on lengths and bond angles, those having a helical form appear to be energetically favored. A 3_1 helix built out of the chemical structure scheme II, and 6_1 helices from the chemical structures III and IV (four loops each), were optimized using the Maximin2 energy optimizer of Sybyl, with the charges from the Gasteiger-Hückel option. The optimized helical structure corresponding to the chemical structure III was found to be the most stable of the three considered. The optimised helices corresponding to the chemical structure schemes II & III are presented in Figure 2. The inter-loop distances vary from 3 Å to 4 Å. It is interesting to note that not all of the torsions are in the same sense, although it is essential for both α and β between two consecutive phenyl rings to be either left-handed or right-handed to keep the steric hindrance to its minimum. Next we used the ASED-MO method to calculate the energies of these Sybyl-optimized structures (the two 6_1 helices were truncated to two loops or to only twelve phenyl rings to facilitate comparisons with the 3_1 helical structure of Figure 2a). No attempt was made this time to optimize the helices using ASED-MO. The total energy of the helix corresponding to the chemical structure III (Figure 2b) was again found to be the lowest in comparison to the two others, in agreement with the Sybyl results. The energies of the rest of the two helices are more or less the same, with the helix of the chemical structure IV slightly more stable than the helix of the chemical structure II. It should be noted that chemical schemes II to IV are only a few of the many possible schemes that could lead to helical structures. For example the next helix would be a 9_1, the

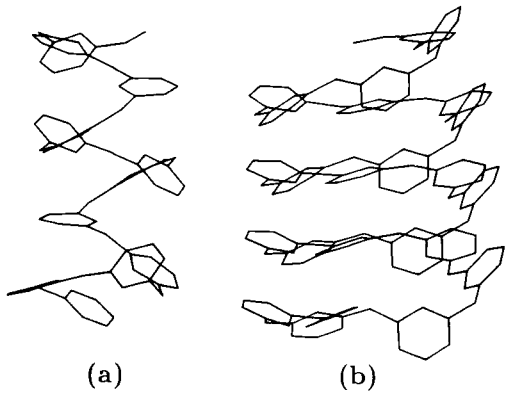


FIGURE 2 (a) A 3_1 helix with four loops, made out of the chemical structure scheme II. (b) A 6_1 helix corresponding to the chemical structure scheme III. Hydrogen atoms and the dots representing the radical nature of the bridging carbon atoms between the phenyl groups have been omitted for clarity.

simplest extension of the scheme IV. The larger the number of phenyl rings in a loop, however, the lower will be the probability for its formation.

ELECTRONIC STRUCTURE CALCULATIONS

In this section we present the electronic structure results, using the ASED-MO method, of the diphenylcarbon radical (Figure 1) and of the Sybyl-optimized helical structures of the chemical schemes II, III and IV (two of which are presented in Figure 2). For the diphenylcarbon radical the π-orbital is located at -10.93 eV. This orbital is singly occupied. The lowest unoccupied molecular orbital (LUMO) is at -8.78 eV, while the highest occupied molecular orbital (HOMO), which is doubly occupied, is at -12.66 eV.

In Figure 3 we have presented the electronic density of states for the helical system of Figure 2b. Twelve phenyl rings and eleven bridging carbon radicals have been considered for this purpose. We have replaced the δ-function energy levels by Gaussian functions of FWHM 0.25 eV. This was done to simulate a larger polymer where the π-, the conduction-, and the valence-bands will form and to take into account the broadening of the lines due to vibrations and other perturbations. The eleven π-orbitals forming the π-band are centered around -10.99 eV and have a combined width of 0.15 eV; they are thus essentially degenerate. Experimental observations[3] of the nonet multiplicity of the chemical structure I lend credence to the idea that the narrowness of the π-and n-bands (see NT) may permit the π- and the n-electrons in these bands to be unpaired. Based on this idea the π-band has been singly occupied with unpaired electrons. We stress here that we have performed no direct calculation of spin-dependent interactions that indicates that the high-spin state is more favorable than the low-spin one. The electronic structure calculations suggest only that the electronic states of the π-electrons form a very narrow band. In addition we expect the electrons to be localized. We

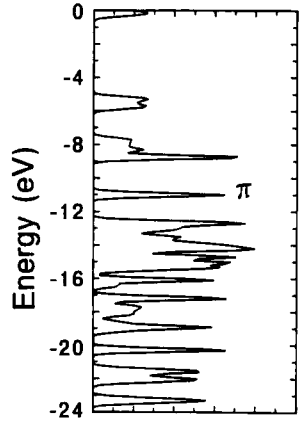


FIGURE 3 The electronic density of states in arbitrary units based on the helical structure of Figure 2(b) with two loops. The δ-function energy levels have been convoluted with Gaussian envelopes of FWHM 0.25 eV to simulate the density of states of a larger polymer and also to take into account the broadening of the lines due to vibrations and other perturbations.

can then argue that the cost in band energy of placing the electrons with parallel spins, and thus completely filling the band, will only be of the order of half the bandwidth, or about 0.1 eV. On the other hand, the lowering in energy due to the exchange contribution obtained by maintaining this parallel spin alignment will be of the order of the Coulomb energy of interaction, which we expect to be appreciably greater. We thus have no complete theoretical justification (but only the */non-* criterion of Ovchinnikov) for expecting parallel spin alignment, but consider the plausibility of such an arrangement to give sufficient motivation for exploring its consequences. The π-band then lies between the bottom of the empty conduction band at −8.82 eV and the top of the completely filled valence band at −12.59 eV.

The electronic density of states for the other two helical structures are very similar. For the structure of Figure 2a, the singly occupied π-band is centered at −10.98 eV with a bandwidth of 0.18 eV. The bottom of the conduction band is at −8.81 eV and the top of the completely filled valence band is at −12.59 eV. The helical structure formed according to the chemical structure scheme IV has the π-band at −10.99 eV with a width of 0.08 eV. The bottom of the conduction band and the top of the completely filled valence band are at −8.85 eV and −12.55 eV, respectively.

All the structures I–IV satisfy Ovchinnikov's */non-* criterion for the topological arrangement of atoms required in order to have the spins on the radical/diradical carbon atoms aligned parallel, and hence to be in a high-multiplet ground state. Because the net angle of bend in structures II, III, and IV is not equal to $2\pi/m$ with m an integer, and also because of the tendency to non-planarity, a large molecule or a polymer will most probably not form a closed ring, but rather will form a helical structure. The dipole interactions, to be discussed shortly, between the spins of different loops of this helical polymer will tend to adjust the structure to cause the spins to be aligned with each other. While the possibility does remain

that these materials may form non-helical structures it seems worthwhile to explore the possible ferromagnetism of such a helical structure.

MAGNETIC STRUCTURE CALCULATIONS

The next task is to study whether a tendency to parallel alignment of the spins on this helix will be likely to yield macroscopic ferromagnetism. If so, what would be the ferromagnetic transition temperature, and how is this Curie temperature affected by the physical and chemical properties of this helix? In Figure 4 we show a schematic diagram of a helix with interacting spins. In addition to the exchange interactions between nearest neighbor spins in a loop of the helix there will also be magnetic dipole-dipole interactions between spins on adjacent loops. We model these interactions in terms of the Ising model[8] for which the Hamiltonian is

$$H = -\sum_{\langle i,j \rangle} J_{ij}\sigma_i\sigma_j - h\sum_i \sigma_i \tag{1}$$

where σ_i and σ_j take values $+1$ or -1 corresponding to spins up or down on sites i and j respectively, J_{ij} is the coupling between this pair of spins, and h is an applied magnetic field. In 1944 Onsager[9] solved this model for an infinite two-dimensional array of spins. With $J_{ij} = \varepsilon$ for nearest neighbors he found that a phase transition occurs at the temperature T for which $\beta\varepsilon = 0.4407$, where $\beta = 1/kT$ and the exchange energy ε is assumed to be the same between the spins in a row or in a column of the array.

We have used this Hamiltonian to study the magnetic susceptibility of an array of spins on radical atoms of a helical polymer, as shown in Figure 4. When one turn of this helix contains only a finite number, m, of spins, no true phase transition will occur, as the system is essentially one dimensional. We do expect to find that the peak in the specific heat as a function of temperature will become sharper with increasing m, finally becoming a phase-transition singularity in the limit $m \to \infty$.

The problem is solved with help of the transfer-matrix approach, which generates

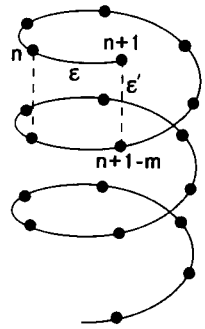


FIGURE 4 Schematic diagram of a helical polymer. The black dots denote radical atoms with unpaired electrons. The quantities ε and ε' are the intra-loop and inter-loop interactions between the spins on these atoms. There are m such atoms per turn of the helix.

the partition function for $n + 1$ spins from the partition function for n spins. For the current problem we have introduced the $(n + 1)^{st}$ spin on a helix of n spins with m spins per turn of the helix (see Figure 4).

The exchange interaction is significant only between the nearest spins on the same loop. Thus the value of J_{ij} is assumed to be non-zero, say ε, for i and j nearest-neighbor sites on the same loop, and zero otherwise. Besides the exchange interaction there would be a relatively weaker long-range dipole-dipole interaction among the spins from the different loops.

At this point it is necessary to discuss the relative orientation of the spins and the helical chain. The intra-loop terms in the Ising Hamiltonian (1) are in reality only an approximation to those in the Heisenberg Hamiltonian, in which the spin-spin interaction is of the form $\vec{S}_1 \cdot \vec{S}_2$. This Hamiltonian does not favor any absolute direction in space, but only requires the magnetic moments to be pointing parallel to each other. The energy contributed by these terms is thus the same for a magnetization along the helical axis as it would be for a magnetization perpendicular to the axis.

The inter-loop terms in (1), on the other hand, are considered not to arise from exchange interactions but from magnetic dipole-dipole forces. These terms are dependent on the orientation in space of the spins relative to the vectors linking near-neighbor spins on adjacent loops of the helix. Because of the low atomic numbers of the atoms constituting this purely organic helix, one would expect negligible anisotropy energy to arise from spin-orbit coupling. The relative strengths of intra-loop and inter-loop dipole-dipole forces will thus be the sole determinant of the direction of magnetization.

To further estimate the distance between consecutive loops of the helix we have computed the energy of interaction of two adjacent layers of structures similar to the ones represented by the chemical structures I to IV. Two methods were used. In the first calculation the ASED-MO energy was computed as a function of the interplanar distance in steps of 0.1 Å, and a minimum found at a separation of 4.2 Å. Because this distance represents an absence of bonding, we also calculated the energy as a sum of van der Waals and Coulomb contributions using the Lennard-Jones parameters suggested by Hopfinger.[10] Now the minimum energy was found at 2.7 Å. Because corrections for finite temperature will increase this value, and because it is known[11] that both graphite and TMPD-PCCp have separations around 3.5 Å we consider a realistic number for the nonbonded interloop separation would be about 3.5 Å. The distance between neighboring spins on the same loop of the helix is about 4.8 Å. The fact that dipole-dipole interaction energies decay as the cube of the distance implies that inter-loop dipole-dipole energies will be stronger than those within the same loop. Although the exchange forces within the loop may be much larger than these dipole forces, the isotropy of the exchange interaction makes these terms irrelevant to a determination of the absolute orientation in space of the magnetic moment. The dipole-dipole forces alone determine the direction of magnetization, and the comparative strength of the inter-loop terms will cause the magnetization to lie parallel to the axis of the helix.

The nature of the dipole-dipole interaction between the neighboring spins on the same loop will be such as to align these spins antiparallel; in other words this

effect is antiferromagnetic. However, a much stronger ferromagnetic exchange coupling between these spins will dominate. The dipole-dipole interaction between the next-nearest-neighbor spins on the same loop is lower by a factor of ~1/8 than that between the nearest-neighbor spins. Thus the effect of dipole-dipole interaction within the loop is to reduce the relatively much stronger ferromagnetic exchange interaction. The dipole-dipole interaction between the nearest spins on the neighboring loops is such as to align these spins parallel. In other words, the nature of this interaction is ferromagnetic. Again the magnitude of this interaction is lower by a factor of ~1/8 for the nearest spins on next-neighboring loops and lower by a factor of $\sim 1/8\sqrt{2}$ for the next-nearest spins on the neighboring loop. Thus, in order to understand the phase transition qualitatively, it should be permissible to simplify the problem to an Ising model in which the interactions J_{ij} are non-zero only for the nearest-neighbor spins. We define $J_{ij} = \varepsilon$ for the nearest-neighbor spins on the same loop, and $J_{ij} = \varepsilon'$ for the nearest-neighbor spins on neighboring loops. The quantity ε' is expected to be weaker than ε by some factor that will be a sensitive function of the geometry of the helix. In the limit of infinitely large m and n (n is total number of spins and m is the number of spins per turn of the helix), one should find the Onsager result for the critical temperature of a two-dimensional square lattice of Ising spins.

The change in energy of the system of n spins due to the addition of the $(n + 1)^{st}$ spin is

$$\Delta H = -\varepsilon\sigma_{n+1}\,\sigma_n - \varepsilon'\sigma_{n+1}\,\sigma_{n+1-m} - h\sigma_{n+1} \tag{2}$$

For a given configuration of $(n + 1 - m)^{th}$ through n^{th} spins, the partition function for $(n + 1)$ spins can be written as:

$$Z(n + 1^{st}\text{ spin}\uparrow) = Z(n\text{ spins})\exp(-\beta\Delta H(\sigma_{n+1}\uparrow))$$

and

$$Z(n + 1^{st}\text{ spin}\downarrow) = Z(n\text{ spins})\exp(-\beta\Delta H(\sigma_{n+1}\downarrow)) \tag{3}$$

where the values of ΔH can be calculated from Equation (2) and depend only on the orientations of $(n + 1 - m)^{th}$ and n^{th} spins. The $(m - 1)$ spins from $(n + 1 - m)$ to n can have 2^{m-1} possible configurations according to whether each spin is up or down. Thus we see that we have a matrix equation

$$Z(n + 1\text{ spins}) = \hat{T}\,Z(n\text{ spins}) \tag{4}$$

where $\hat{T}$ is the transfer matrix and is of order $2^m \times 2^m$ with every row and every column having only two non-zero matrix elements $\exp(-\beta\Delta H)$ corresponding to the two nearest neighbors n and $n + 1 - m$ of the spin $n + 1$. Now the problem is reduced to finding the eigenvalues of this transfer matrix $\hat{T}$. In the thermodynamic limit, when $n \to \infty$,

$$\ln Z_{n+1} = (n + 1)\ln\lambda_{max} \tag{5}$$

where λ_{max} is the largest eigenvalue of the matrix $\hat{T}$. Thus the Helmholtz free energy per spin is

$$F = -k\mathrm{T} \ln \lambda_{max} \tag{6}$$

from which the other thermodynamic functions are readily evaluated. These are calculated either at constant temperature, T, or at constant external magnetic field, h. The magnetization is given as

$$M = -\left(\frac{\partial F}{\partial h}\right)_{\mathrm{T}},$$

the isothermal susceptibility is

$$\chi_{\mathrm{T}} = \left(\frac{\partial M}{\partial h}\right)_{\mathrm{T}},$$

the entropy is

$$S = -\left(\frac{\partial F}{\partial \mathrm{T}}\right)_{h},$$

and the specific heat at constant magnetic field is

$$C_H = \mathrm{T}\left(\frac{\partial S}{\partial \mathrm{T}}\right)_{h}.$$

The susceptibility, χ_{T}, and the specific heat, C_H, can both be calculated by evaluating the second derivative of the free energy, one with respect to the magnetic field, h, and the other with respect to the temperature, T. For an infinite system, i.e. for both n and m approaching infinity, $\chi_{\mathrm{T}}(\lim h \to 0)$ and $C_H(\lim h \to 0)$ both diverge at the critical temperature T_c, with χ_{T} then varying as $(|\mathrm{T} - \mathrm{T}_c|/\mathrm{T}_c)^{-7/4}$ while the divergence in the specific heat, C_H, is only logarithmic.[12] Our numerical results for finite m reflect this difference, the peak found for χ_{T} being sharper than that found for C_H.

It is convenient to work with the dimensionless temperature, τ $(=k\mathrm{T}/\varepsilon)$, and with the dimensionless field, h/ε. For zero external field ($h = 0$), we define τ_c as the dimensionless temperature at which C_H is a maximum and have evaluated $C_H(\tau_c)$ and the width $\Delta\tau$ of $C_H(\tau)$ at half height for $\varepsilon' = \varepsilon$ and for $\varepsilon' = \varepsilon/5$ for values of m ranging from 2 to 9. These results are presented in Figures 5 and 6. For $\varepsilon' = \varepsilon$ and for $m \to \infty$, the helix would be equivalent to a 2-dimensional square lattice and as such $\tau_c(m \to \infty)$ should approach the Onsager value of $\tau_c^{\infty} = 2.2692$. From Figure 5 it is clear that for large m, the numerically obtained τ_c seems to be approaching τ_c^{∞}. The half width of the C_H becomes smaller as m increases, as expected. The temperatures τ_1 and τ_2 at which C_H has half its maximum height converge on τ_c as m is increased, and appear to extrapolate to give a vanishing

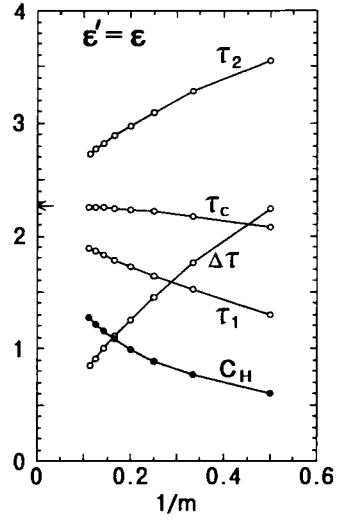


FIGURE 5 The dimensionless critical temperature τ_c, as a function of $1/m$ for a helix of m (=2 to 9) spins with the same inter-loop interaction ε', and intra-loop interaction, ε, and for zero external field. The arrow denotes Onsager's analytic result corresponding to $m = \infty$. Other quantities plotted are the specific heat, C_H, (in arbitrary units) at τ_c, the width, $\Delta\tau$, of the specific heat, and the positions, τ_1 and τ_2 where the specific heat has half its peak value.

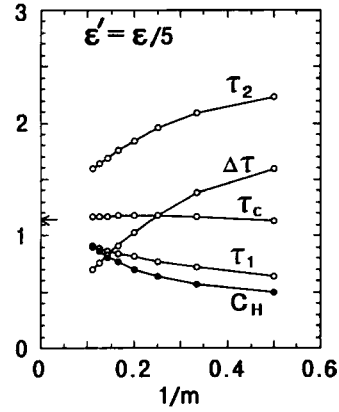


FIGURE 6 Same as Figure 5, but for $\varepsilon' = \varepsilon/5$.

value of $\Delta\tau$ as $m \to \infty$. For $\varepsilon' = \varepsilon/5$, i.e. when the inter-loop dipole-dipole interaction is weaker than the intra-loop exchange interaction one finds a reduction in τ_c by about a factor of two. In this case τ_c^{∞} is 1.1416, a result obtained by equating $\sinh 2\beta\varepsilon \times \sinh 2\beta\varepsilon'$ to unity.[13]

In order to examine the magnetic properties, we now apply an external magnetic field and study the magnetization and susceptibility as functions of magnetic field and temperature. The results for magnetization of a helix with $m = 6$ are presented in Figures 7 and 8 for $\varepsilon' = \varepsilon$ and $\varepsilon' = \varepsilon/5$ respectively. Similar results are obtained for other values of m in the range $3 \leq m \leq 9$, at which the structures of type II to IV are expected to form.

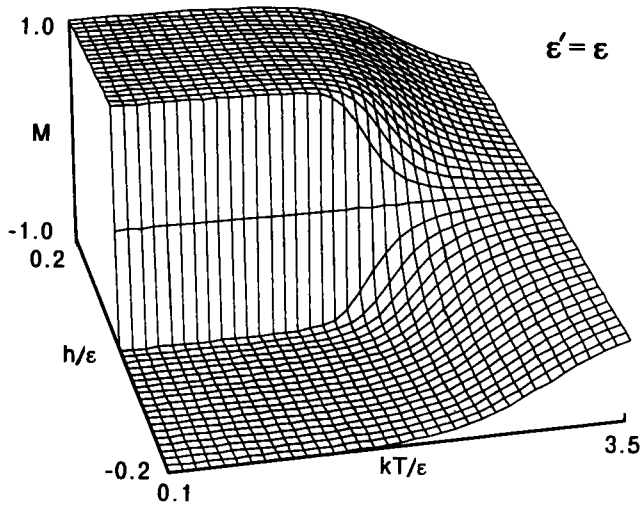


FIGURE 7 Magnetization of the helix with $m = 6$ for $\varepsilon' = \varepsilon$ as a function of dimensionless temperature and dimensionless magnetic field.

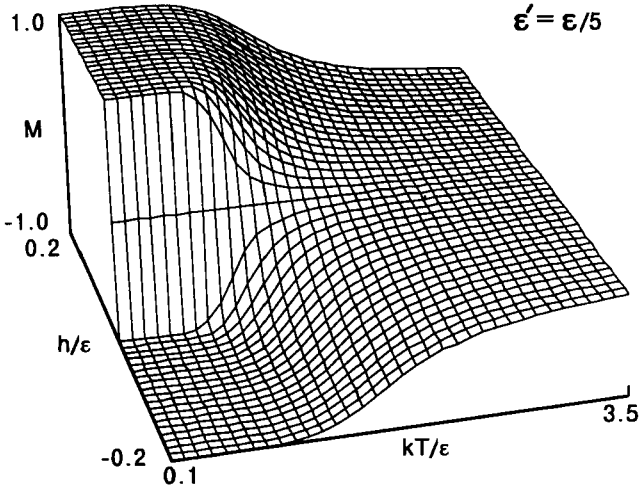


FIGURE 8 Same as Figure 7, but for $\varepsilon' = \varepsilon/5$.

The cooperative effect of the spins in the helical structure is readily apparent in Figures 7 and 8. As the temperature is lowered below the range at which the specific-heat-maximum temperature T_c occurs, one observes a rapid rise in the magnetization at weak applied fields. Comparison of these two figures shows that a lowering of the inter-loop interaction ε' by a factor of five causes a reduction of T_c by a factor of about two.

Because the helix is essentially a one-dimensional entity, the magnetization remains zero when the applied field h is identically zero; however, a field h of magnitude less than $10^{-2}\ \varepsilon$ is sufficient to saturate the magnetization at all tem-

peratures appreciably below T_c. The giant susceptibility will have the consequence that only very weak inter-helix interactions will be required in order for spontaneous ferromagnetism to occur.

SUMMARY

The electronic structure of certain compounds indicates the possibility of purely organic polymer ferromagnets. Some π-bonded hydrocarbons have their radical/diradical orbitals lying between a filled valence band and an empty conduction band. These orbitals form a very narrow half-filled band where electrons are expected to be unpaired. The topological arrangement of atoms is important in these materials if the spins of these electrons are to be aligned parallel. We have studied the magnetization of a helical polymer within the framework of the Ising model. The magnetization, the critical temperature and the specific heat have been calculated for helices having various numbers of spins per loop for two values of the ratio of inter-loop to intra-loop interaction. A peak in the zero-field specific heat and saturation in the low-temperature magnetization in the presence of small but non-zero magnetic fields suggest that macroscopic ferromagnetism might occur in a bulk sample of these materials.

Acknowledgments

We are grateful to R. B. Adkins, B. Frank, and R. G. Petschek for helpful advice and discussion. This research has been supported by grant No. N00014-88K-0631 from the U.S. Defense Advanced Research Projects Agency, and grant No. DMR89-02220 from the U.S. National Science Foundation. Computing resources were provided by the Ohio Supercomputer Center and by the Edison Polymer Innovation Corporation.

References

1. K. Itoh, *Chem. Phys. Lett.*, **1**, 235 (1967); K. Itoh, H. Konishi, and N. Mataga, *J. Chem. Phys.*, **48**, 4789 (1968).
2. T. Takui and K. Itoh, *Chem. Phys. Lett.*, **19**, 120 (1973).
3. Y. Teki, T. Takui, K. Itoh, H. Iwamura and K. Kobayashi, *J. Am. Chem. Soc.*, **105**, 3722 (1983); T. Sugawara, S. Bandow, K. Kimura, H. Iwamura and K. Itoh, *J. Am. Chem. Soc.*, **108**, 368 (1986).
4. K. Nath and P. L. Taylor, *Mol. Cryst. Liq. Cryst.*, **108B**, 389 (1990).
5. A. B. Anderson, *J. Chem. Phys.*, **62**, 1187 (1975); A. B. Anderson, R. W. Grimes and S. Y. Hong, *J. Phys. Chem.*, **91**, 4245 (1987).
6. K. Nath and A. B. Anderson, *Solid State Commun.*, **66**, 277 (1988); *Phys. Rev. B.*, **41**, 5652 (1990).
7. A. A. Ovchinnikov, *Dokl. Akad. Nauk SSSR*, **236**, 928 (1977); *Theoret. Chim. Acta (Berl.)*, **47**, 297 (1978).
8. E. Ising, *Z. Phys.*, **31**, 253 (1925). For a comprehensive review of the Ising model, see C. Domb in "Phase Transitions and Critical Phenomena" vol. 3, editors C. Domb and M. S. Green (Academic Press, London, 1974).
9. L. Onsager, *Phys. Rev.*, **65**, 117 (1944).

10. A. J. Hopfinger, "Conformational Properties of Macromolecules" (Academic Press, New York, 1973).
11. T. P. Radhakrishnan, Z. G. Soos, H. Endres, and L. J. Azevedo, *J. Chem. Phys.*, **85**, 1126 (1986).
12. H. E. Stanley, "Introduction to Phase Transitions and Critical Phenomena" (Oxford University Press, New York, 1971).
13. B. M. McCoy and T. T. Wu, "The Two-Dimensional Ising Model" (Harvard University Press, Cambridge, MA, 1973).