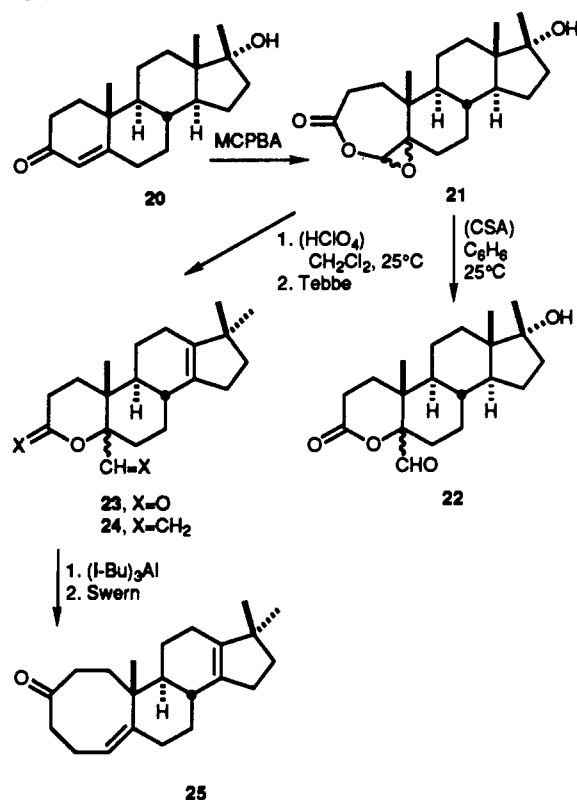


Scheme V



only one unusual characteristic, viz., its rate was approximately 20 times slower than that of **4**. As will be shown, this kinetic retardation is not due to the presence of added oxygen functionality, but to the proximal angular methyl group, presumably because of the added steric encumbrance it brings to the Claisen transition state.

Manool (**10**) has also served as a starting point for implementation of the intercalation process (Scheme III). Conversion of **10** to epoxy lactone **11**¹³ set the stage for isomerization to **12** (2 M NaOH, MeOH; dilute HCl; 100%) and 2-fold methylenation (64% of **13**). In an informative experiment, exposure of **13** to 10 equiv of Tribal in CH_2Cl_2 resulted in completion of the desired ring expansion within 15 min at room temperature. As in **4**, the sigmatropic process is facilitated by the absence of an alkyl group at the proximal angular site.

Most indicative of the synthetic versatility of this methodology are the results achieved with testosterone (**15**) and its 17 β -methyl homologue **20**. Following silylation of **15** (95%), oxidation with MCPBA¹⁴ was effected as before (85%) and the stereoisomeric mixture was isomerized to **17** (94%) with a catalytic amount of *d*-camphor-10-sulfonic acid in benzene at 25 °C (Scheme IV). The ensuing Tebbe reaction, performed under the standard conditions, furnished **18** efficiently (92%) as a prelude to the ring expansion. In the presence of a solution of excess Tribal (5 equiv) in CH_2Cl_2 , the Claisen rearrangement of **18** required 6 h to go to completion (compare **13**). Swern oxidation of the resulting cyclooctenol (64% isolated) afforded **19** (82%).

The hydroxyl group in **20**, unlike **15**, was left unprotected (Scheme V). Peracid oxidation furnished **21** (70%), an intermediate that could be isomerized to **22** without dehydration of the tertiary carbinol, or to **23** via carbocation formation, Wag-

ner-Meerwein shift, and ultimate dehydration (88%). The availability of **23** in this manner made possible the acquisition of **25** in good overall yield (**23** \rightarrow **24**, 93%; (*i*-Bu)₃Al, 63%; Swern, 78%). That the Claisen rearrangement of **24** required 6 h at 25 °C for completion is further substantiation of the rate-retarding steric role played by the angular methyl substituent.

The methodology herein described provides the groundwork and incentive for considerable further experimentation. It is our intention to report on further studies in this area and some interesting synthetic applications at a future time.¹⁵

(15) The financial support of this work by the National Institutes of Health (Grant GM-30827) is gratefully acknowledged.

Novel Magnetic Properties of a Doped Organic Polymer. A Possible Prototype for a Polaronic Ferromagnet

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Received August 13, 1990

There are many approaches to the preparation of organic materials with novel magnetic behaviors.¹ Of these, perhaps the least explored has been the "polaronic ferromagnet", christened by Fukutome in a recent theoretical work.² We describe here an initial experimental approach to such a structure and evidence for significant *ferromagnetic couplings* in the material.

The general approach to magnetic organic materials that we have been pursuing is schematized in the drawing.³ In the polaronic ferromagnet, the spin-containing moiety is a polaron: the partially delocalized radical cation (anion) that one obtains on oxidative (reductive) doping of a conjugated polymer. Using a Wittig polymerization route described previously,^{3b} we have prepared the octadecyloxy substituted poly(*m*-phenyleneoctatetraene) derivative PMPOT-18.⁴ The key design features are (1) *m*-phenylene as the ferromagnetic coupling unit;⁵ (2) a tetraene as the easily oxidized "polaron" precursor; and (3) *O*-alkyl groups to enhance polymer solubility. Concerning the last point, PMPOT-18 is soluble in a variety of organic solvents and forms

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(4) PMPOT-18: MW by GPC (toluene, 40 °C; polystyrene standard): $M_N = 6130$; $M_W = 15800$ (monomer weight 449); ¹H NMR (CDCl₃) δ 0.85 (m, 3 H), 1.28 (br s, 30 H), 1.43 (br s, 2 H), 1.78 (br s, 2 H), 3.9 (br s, 2 H), 6.4-6.8 (br, 11 H); IR (thin film, cm⁻¹): 680 (m), 972 (m), 998 (s), 1465 (s), 1568 (s), 2852 (s), 2922 (s), 3018 (m); UV (CHCl₃) $\lambda_{max} = 400$ nm, additional peak at 422 nm, sh at 382 nm. Films for doping were ca. 90 μ m thick. Elemental anal. Calcd for C₃₂H₅₀O: C, 85.27; H, 11.18; O, 3.55. Found: C, 84.24; H, 10.72; O, 4.22; Br, 0.18; P, 0.27.

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(14) For earlier applications of this oxidation to steroids and diterpenes, see: (a) References 5 and 13. (b) Gorodetsky, M.; Danieli, N.; Mazur, Y. *J. Org. Chem.* **1967**, *32*, 760. (c) Chang, C. W. J.; Pelletier, S. W. *Tetrahedron Lett.* **1966**, 5483. (d) Pelletier, S. W.; Chang, C. W. J.; Iyer, K. N. *J. Org. Chem.* **1969**, *34*, 3477. (e) Abad, A.; Agulló, C.; Arnó, M.; Cuñat, A. C.; Zaragozá, R. J. *J. Org. Chem.* **1989**, *54*, 5123.

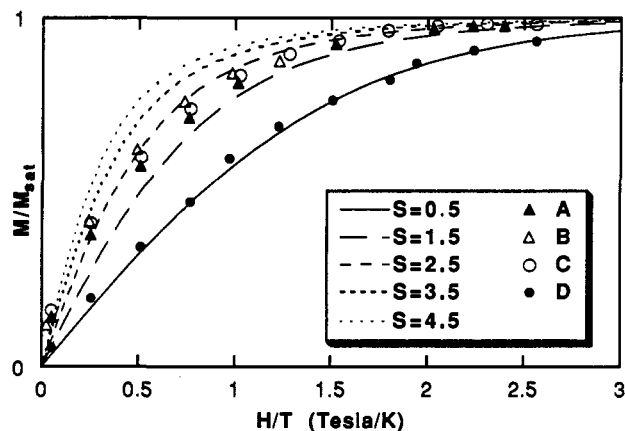


Figure 1. Plots of normalized magnetization (M divided by the saturation value, M_{sat}) for various PMPOT-18 samples doped with AsF_5 . Lines represent theoretical curves for indicated values of S according to the Brillouin function. Experimental points are for different samples, as follows: A, lightly doped PMPOT-18 at 2 K; B, same sample as in A but at 4 K; C, a second sample of lightly doped PMPOT-18 at 2 K; D, sample C after further doping ("heavily doped") at 2 K. Magnetizations were measured by using an SHE SQUID magnetometer.

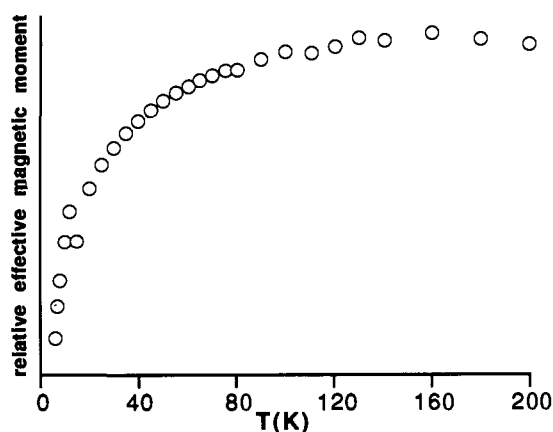
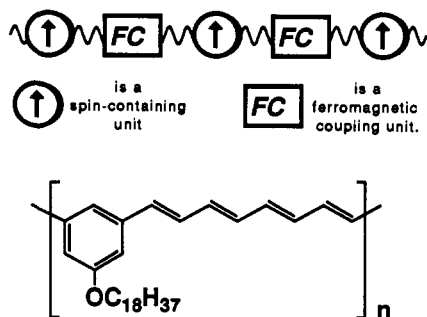


Figure 2. Plot of relative effective magnetic moment (i.e., square root of the product of χ_g (emu/g) and T) vs temperature for sample C of Figure 1.

free-standing, transparent, yellow films. This allows a complete characterization of the material and an unambiguous determination of its structure.



PMPOT-18

For magnetization studies, we have focused on PMPOT-18 films that are lightly doped^{6,7} with AsF_5 . The doping is performed at

(6) Assuming that AsF_6^- is the counterion⁸ and determining the number of spins from the saturation value of M gives the following: "lightly" doped, 8 monomers/counterion, 222 monomers/spin; "heavily" doped, 0.2 monomers/counterion, 29 monomers/spin. The doped materials are insoluble. Their color darkens and they become increasingly brittle as the doping proceeds.

(7) Similar behavior is also seen in samples doped with I_2 .

room temperature, and EPR studies demonstrate that spins introduced by doping are long-lived at room temperature. Figure 1 shows plots of the normalized magnetization induced in such samples upon application of an external magnetic field (H).⁹ Clearly the system does not display $S = 1/2$ behavior, which would be expected if only isolated polarons were produced. Instead, $S \geq 2$ behavior is seen, establishing the existence of significant net ferromagnetic couplings in the system.

There is also a weak antiferromagnetic interaction in the solid, indicated by the downturn at low temperatures in the relative effective magnetic moment plot of Figure 2.¹⁰ This explains why the 4 K data of Figure 1 generally correspond to a higher S value than the 2 K data. Importantly, when a lightly doped sample that displays $S > 2$ behavior is then heavily doped⁶ with AsF_5 , the value of M_{sat} (i.e., the spin concentration) increases, but the apparent S decreases to ca. $1/2$ (Figure 1). This establishes that the high-spin behavior we see is not a consequence of some impurity introduced by the dopant.¹¹ We assume that extensive doping degrades the material, thus destroying the ferromagnetic coupling. As controls, poly(*p*-phenylenevinylene) and poly(*p*-phenyleneoctatetraene) were synthesized and doped in manners similar to PMPOT-18, and they display the expected $S \leq 1/2$ behavior.

To rationalize these observations, we propose the following model. It is well-known that doping of conjugated polymers by agents such as AsF_5 can be quite inhomogeneous,^{8,12} and it is clear that this is the case in the present system. The number of spins introduced is small enough⁶ that, were they evenly distributed throughout the material, it is highly unlikely that any significant magnetic interactions could develop among them. Instead, there must be regions of relatively heavier doping that allow significant overall ferromagnetic coupling of spins. These ferromagnetic interactions must be fairly strong, since they persist to at least 200 K (Figure 2). While it is tempting to ascribe them to one-dimensional, *intramolecular* couplings along the chains mediated by the *m*-phenylene coupling units, further work will be required to verify this.

Along with the ferromagnetic coupling, there is also a weak, antiferromagnetic interaction that becomes evident only at very low temperatures (Figure 2). We interpret this as resulting from *intermolecular* coupling between chains, which would be expected to be antiferromagnetic. The S we see is thus a composite, resulting from the combination of the strong ferromagnetic interaction and the weak antiferromagnetic interaction. Note also that, on the basis of the results of Figure 2, the S value of the doped material should substantially increase at higher temperatures, where the weak antiferromagnetic coupling would be overcome by thermal energy.

To summarize, the rationally designed and synthesized polymer PMPOT-18 can be oxidatively doped to a state that displays significant ferromagnetic interactions among paramagnetic centers introduced by the doping. If, as we propose, this is a consequence of one-dimensional ferromagnetic couplings along the polymer backbone, these results indicate that the polaronic ferromagnet could represent a promising approach to the preparation of magnetic organic materials.

Acknowledgment. We thank Professor Chris Reed and Robert Ortz of USC for assistance with the SQUID measurements and Professor Robert Grubbs of Caltech for helpful discussions. This

(8) See, for example: Masse, M. A.; Composto, R. J.; Jones, R. A. L.; Karasz, F. E. *Macromolecules* 1990, 23, 3675-3682 and references therein.

(9) See, for example: Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, 1986. Gerlock, M. *Magnetism and Ligand-Field Analysis*; Cambridge University: New York, 1983. Mabbs, F. E.; Machin, D. J. *Magnetism and Transition Metal Complexes*; Chapman and Hall: London, 1973.

(10) A Curie-Weiss plot for lightly doped material is linear for $T < 150$ K and produces a Weiss constant of -6 K, consistent with weak, antiferromagnetic interactions.

(11) The magnetization behavior of Figure 1 is *not* that of a ferromagnet. Thus, the spins we see do not result from trace amounts of Fe or other ferromagnetic impurities.

(12) See, for example: Pekker, S.; Jánosy, A. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. I, pp 45-79.

work was supported by the Caltech Consortium in Chemistry and Chemical Engineering (founding members: E. I. du Pont de Nemours and Company, Inc., Eastman Kodak Company, and Minnesota Mining and Manufacturing Company) and by the Office of Naval Research.

Registry No. PMPOT-18, 131216-26-7; AsF₅, 7784-36-3.

Gas-Phase Charge-Transfer Reactions and Electron Affinities of Macrocyclic, Anionic Nickel Complexes: Ni(SALEN), Ni(tetraphenylporphyrin), and Derivatives

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Received October 9, 1990

Revised Manuscript Received January 23, 1991

We describe here the gas-phase reactions of radical anions of several Ni complexes of tetradentate ligands. The neutral complexes are 16-electron metal complexes, and the corresponding anions are 17-electron species. We have found that facile electron transfer to an organic electrophile is characteristic of these species and that in some cases it is possible to observe reversible electron-transfer reactions. In these cases the electron affinity (EA) of the complex can be determined from the equilibrium constant of the charge-transfer reaction and the EA of the electrophile. We report several such electron affinities here and believe these to be the first gas-phase electron affinities for such species.

These measurements are made possible by the availability of Fourier transform ion cyclotron resonance techniques.¹ Because of the very long ion trapping time, it is possible to examine reactions of ions with neutral species of very low vapor pressure. Also critical to these measurements is the reliable gas-phase electron affinity scale which was developed by equilibrium constant measurements by Fukuda and McIver² and Kebarle et al.³ and photodetachment studies of SO₂ by Cellota, Bennett, and Hall.⁴ We use the numbers given by Kebarle in a recent review.³

Ni(SALEN) (1) prepared by methods in the literature^{5,6} was introduced into the vacuum system of an FT-ICR instrument (FTMS-2000,⁷ Extrel, Madison, WI) on a heated probe. An electrophile such as nitrobenzene was introduced through the batch inlet system. The two species at a combined nominal pressure of $\sim 10^{-7}$ Torr were exposed to a 5-ms pulse of a nominal 4-eV electron beam. The radical parent ions of both neutrals were formed by attachment of scattered electrons caught in the trap. The intensities of the ion signals were monitored as a function of delay after the electron beam pulse. When the total ion signal stopped increasing, indicating that all electrons in the trap had been consumed by attachment, one of the ions was ejected. After the ejection, the reversible electron transfer was allowed to come to steady state. The product of the ratio of the steady state ion signals and the ratio of the neutral pressures was taken as the equilibrium constant for charge transfer. Throughout these studies the ratio of neutral pressures was estimated from the electron-

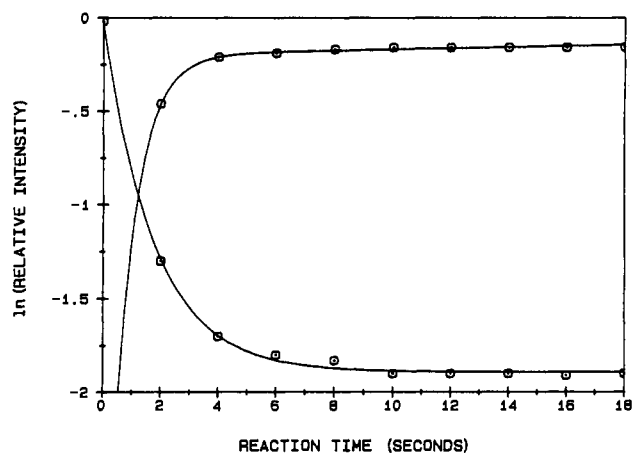
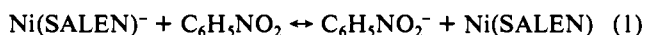


Figure 1. The variation with time of Ni(SALEN)⁻ and nitrobenzene anion in a mixture of the two neutrals following ejection of Ni(SALEN)⁻ from the trap. The Ni(SALEN)⁻ increases and nitrobenzene anion decreases as a result of a reversible electron transfer which eventually comes to equilibrium.

impact mass spectrum of the mixture and the relative ionization cross sections of the components.⁸ The final equilibrium constants were found to be independent of which ion was ejected and independent of pressure. A typical result for reaction 1 is illustrated in Figure 1. Assuming that $\Delta G = \Delta H^\ddagger$ for reaction 1 and taking



the electron affinity of C₆H₅NO₂ as 1.01 eV gives EA[Ni(SALEN)] = 1.06 ± 0.01 eV. This is strikingly similar to EA[Ni(CO)₃] = 1.08 eV.⁹

Both Ni(CO)₃¹⁰ and Ni(CO)₃⁻¹¹ are planar; so are Ni(SALEN) and Ni(SALEN)⁻. This structural similarity combined with the similarity in EAs suggests that the two anions have similar singly occupied orbitals. This in turn suggests that the added electron in the singly occupied orbital in Ni(SALEN)⁻ is not substantially delocalized into the ligand.

Ni(SALEN)⁻ was found not to react with CH₄, CH₃I, C₆H₁₂, CH₃OH, or (CH₃)₂C=O. The upper limit on the rate constants is about 1.5 × 10⁻¹³ cm³ s⁻¹. This is in contrast to a previous report that Ni(SALEN)⁻ reacts with CH₄ and *i*-C₄H₁₀.¹² The earlier work involved reactions in a CH₄ plasma at 1 Torr total pressure. Such a plasma contains a variety of radicals which probably react to produce the ions attributed to CH₄ reaction.

On heating of Ni(SALEN) on the probe, a peak corresponding to the loss of H₂ from Ni(SALEN) appeared in both positive- and negative-ion mass spectra. The relative intensity of the peak increased with temperature, indicating a thermally activated loss of H₂ from the neutral. The peak was attributed to a species with structure 2 as the most thermodynamically favorable H₂ loss product of Ni(SALEN) (1). This process provided an opportunity to determine the EA of 2. Electron transfer between 2 and maleic anhydride and between 2 and 4-bromonitrobenzene is reversible, and from equilibrium constant measurements for these processes, it was found that EA(2) = 1.37 ± 0.01 eV. The substantial

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